APPENDIX H

PETROLEUM REFINERY FLUID CATALYTIC CRACKING UNITS

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APPENDIX H

PETROLEUM REFINERY FLUID CATALYTIC CRACKING UNITS

H-1.0 INTRODUCTION

The seven major, and one smaller, oil refineries in the Basin operate eight fluid catalytic cracking (FCC) units. Of the total product processed, 25 to 40% passes through these units. Offgas from the process contains sulfur released from coke burned in reactivation of the cracking catalyst. This gas, low in oxygen content and with high CO levels, is passed through a waste gas boiler in which excess air is added and a flame sustained to complete combustion of the CO. The resultant CO boiler stack emissions are the largest source of SOx emissions in refineries and follow utility boilers as the second largest source of SOx emissions in the Basin.

Emissions of SOx are directly related to sulfur content in the coke burned off the catalyst and if coke burning rate and sulfur content are known, emissions can be treated in a manner similar to fuel combustion sources. However, the coke formation rate is a complex function of the many unit operating variables. Furthermore, coke sulfur content is only approximately related to feed stock sulfur content. It is thus impractical, in the absence of access to highly proprietary process data, to attempt any predictive estimate of SOx emissions without source test data. Even with source test results available, the application of that data for prediction of emissions over any extended period of time with changing crude properties and process adjustments, can only result in estimates that have a high level of uncertainty. However, sufficient information outside the proprietary domain is available to allow fairly reasonable estimates of the boundaries of possible emissions as a guide to the main objective of emissions control. Furthermore, recent developments at one U.S. refinery have demonstrated an effective method of flue gas desulfurization that should be applicable for cost effective SOx emissions control for the Basin's FCC units.

The following sections describe the FCC process as related to SOx emissions, present results of tests conducted on 6 of the 8 Basin FCC units during the current program, the inventory of SOx emissions, and assessment of reduction potential.

H-2.0 REFINERY FCC UNIT PROCESS DESCRIPTION

The petroleum refining process begins with atmospheric distillation of the crude feed stock into volatile fractions for separate further processing. The heaviest portion of the crude does not vaporize in this process as evaporation temperatures exceed the point at which thermal cracking would occur. Further distillation of this crude residuum is performed under a vacuum and separated into heavy vacuum gas oil and asphaltic material. The latter is processed in a coker to form the petroleum coke that is calcined in kilns as discussed in Appendix K. The vacuum gas oil is suitable for conversion to gasoline and other products by means of cracking. A cracking process is one in which high molecular weight hydrocarbon molecules are split into molecules of lower molecular weight that are thus more readily converted to gasoline by various other processes. The cracking can be done by thermal, hydro or catalytic cracking and it is the latter for which fluid catalytic cracking units are employed.

One important point of note in digression is that it would appear that the refining process is a continuously flowing stream with crude entering one end and products with properties identified with the crude exiting the other. This is not the case in actuality. Large pool storage areas are used to collect partially processed crudes and the gas oil that arrives at the point for catalytic cracking may be a mixture of the results of processing several crude types that may have entered the refinery at various times. Therefore, knowledge of the property of the crude entering the refinery at any given point in time does not necessarily provide a clear cut picture of the gas oil entering the cracking process at that point or any point at a later time. Conversely, analysis of a gas oil sample taken, for example, during a source emission test may, not necessarily allow any conclusions to be drawn regarding the classification of a crude type from which this gas oil might have originated. This fact also has wider implications for any attempt to establish a mass balance of refinery sulfur input and output.

The cracking process as performed in an FCC starts with partial vaporization of the gas oil feed and injection with steam into a stream of hot silica-alumina catalyst at about 800-1000°F. As illustrated in Figure H-1, this mixture rises through a cracking "riser" and enters a large reaction vessel where cracking is completed and catalyst separated from the product vapors. Product vapors are extracted from the top of this reactor vessel. During the cracking process part of the gas oil, typically about 6% by weight, is, deposited on the catalyst powder as high carbon coke. This deposition sharply reduces catalyst activity and the coke must be burned off. To accomplish this, the catalyst stream flows out of the bottom of the reactor to another large vessel called the regenerator.

At the point of catalyst extraction from the reactor steam is injected, called "stripping steam" for the purpose of driving separable hydrocarbons off the coke and catalyst. This function has been identified as a potential means for sulfur oxides emission reduction (Ref. 14). Sulfur in the form of H_2S will tend to be stripped by the steam along with the hydrocarbons. The H_2S then exits the reactor in the steam rather than on the catalyst. The H_2S stripped from the coke can then be removed along with the H_2S from other processes in the normal refinery H_2S treatment systems. However, stripping steam requirements to extract sulfur are much greater than normally required for hydrocarbon stripping. This technique is discussed further in Section H-5.

On leaving the steam stripper, the catalyst flows to the regenerator where the coke is burned off the catalyst. Air is fed into the bottom of the regenerator and flows upward through the catalyst. Burning the coke serves a second purpose of providing the heat necessary to maintain the entire process at the required cracking temperature. Complete combustion of the coke would result in excessive temperatures damaging the catalyst so air is restricted below the theoretical requirement. The coke contains carbon, hydrogen, sulfur and other elements. The carbon and hydrogen contents are of the order of 90% and 10%, respectively, with sulfur content varying as a function of, but not equal to, the sulfur content of the feed. Combustion of this coke in a

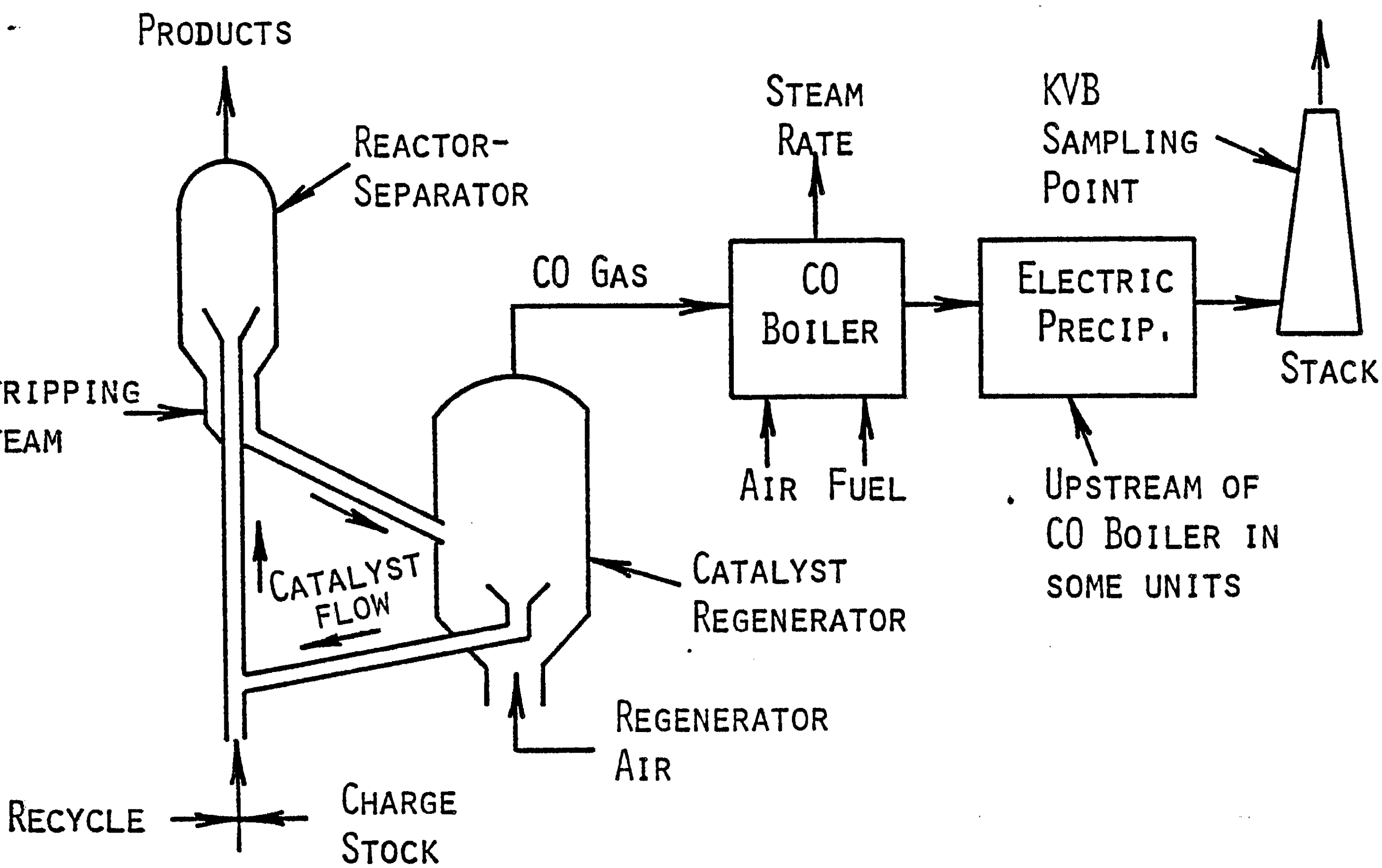

FIGURE H-1. FLUID CATALYTIC CRACKING UNIT PROCESS SCHEMATIC.

deficiency of air results in complete combustion of the hydrogen and sulfur but only partial oxidation of the carbon.

The regenerated and heated catalyst exits the bottom of the regenerator to return to the starting point of feed injection. Combustion products exit at the top and, prior to the advent of air pollution controls, were emitted to the atmosphere. For all FCC units in the Basin, CO and particulate controls have been implemented in the form of waste heat recovery boilers to combust the CO and electrostatic precipitators to extract particulates. These devices have no effect on sulfur oxides emissions, except that additional fuel for flame stabilization, burned in the CO boiler, will add additional SOx.

In the absence of excess air, the sulfur oxide formed is directly related to the coke properties and the level of CO formed by (Ref. 14):

$$(SOx)_F = \frac{S \times 10^6}{2.667 + 5.015\frac{(2R + 1)}{(R + 1)}(1 - S - H) + 27.43 H + 2.095 S} \qquad \text{H-1}$$

where: $(SOx)_F$ = SOx concentration in FCC exhaust, volume parts per million, dry basis

S = Weight fraction of sulfur in coke

H = Weight fraction of hydrogen in coke

R = % volume CO_2/% volume CO in FCC exhaust

In this equation, $R = 0$ if all carbon is as CO and $R = \infty$ if all carbon is as CO_2. FCC units normally operate with a value of R of 1 to 2. Introduction of excess air in a CO boiler will reduce the concentration of SO_2 by: (neglecting fuel added in the boiler):

$$(SOx)_S = (SOx)_{F\; R=\infty} \; \frac{21 - O_{2S}}{21} \qquad \text{H-2}$$

where: $(SOx)_S$ = CO boiler stack SOx, ppm dry

$(SOx)_F$ = ppm SOx, equation H-1 for $R = \infty$

O_{2S} = CO boiler stack percent oxygen, dry

For an assumed typical coke hydrogen content of 10% (Ref. 14) at nominal sulfur contents, the SOx concentration from the CO boiler stack is:

$$(SOx)_S = 69500\left(\frac{21 - O_{2S}}{21}\right) \quad S \qquad \text{H-3}$$

For a typical O_2 level of 1.5%, Equation H-3 indicates that an SOx concentration of 500 ppm would be reached at a coke sulfur content of S = 0.0077 or 0.77% sulfur by weight. The foregoing equations also hold for fuel combustion and for 0.5% sulfur oil with a typical oil hydrogen content of 12%, the SOx concentration would be 315 ppm at 1.5% O_2, (Constant in Equation H-3 becomes 67820.) The relations expressed by Equations H-1 to H-3 are illustrated in Figure H-2. This shows that the regulation of 0.5% sulfur fuel is more stringent than a 500 ppm rule would be for FCC units. Current SOx regulations in the Basin vary from 300 ppm in Ventura to 2000 ppm in Los Angeles County. FCC coke would have to be lowered in sulfur content to about 0.48% sulfur by weight to meet a concentration level equal to burning 0.5% sulfur oil.

The foregoing relations are quite straightforward when compared with the relation of coke sulfur to feed stock sulfur and implications drawn for feed desulfurization. If coke sulfur were always equal to feed sulfur and desulfurization of the feed produced an equal reduction in coke sulfur, then it would only be necessary to desulfurize the feed to an 0.77% level to meet a 500 ppm regulation or to 0.48% for equivalence to 0.5% S oil. This assumption was made in Ref. 14 in evaluation of various methods of FCC SOx control based on information that coke sulfur varied only between 0.7 and 1.2 times feed sulfur. Data published by Gulf Research and Development shows that the variation is more like 0.5 to 3 times as shown in Figure H-3 extracted from data in Ref. 88. These data were taken with a 2 barrel/day pilot plant reported to operate closely to actual FCC units. The figure shows that West Texas gas oil at 2% sulfur must be desulfurized to 0.2% to meet a coke sulfur level of 0.48% (315 ppm). California gas oil on the other hand at 1.2% sulfur yields only 0.6% sulfur coke with no desulfurization. The result is that for a given feed stock sulfur content, coke % S can vary over a range of .5 to 3 relative to feed sulfur and by the direct relation the same variation will occur in SOx emissions. The reason for this effect is undoubtedly related to the molecular form by which the sulfur

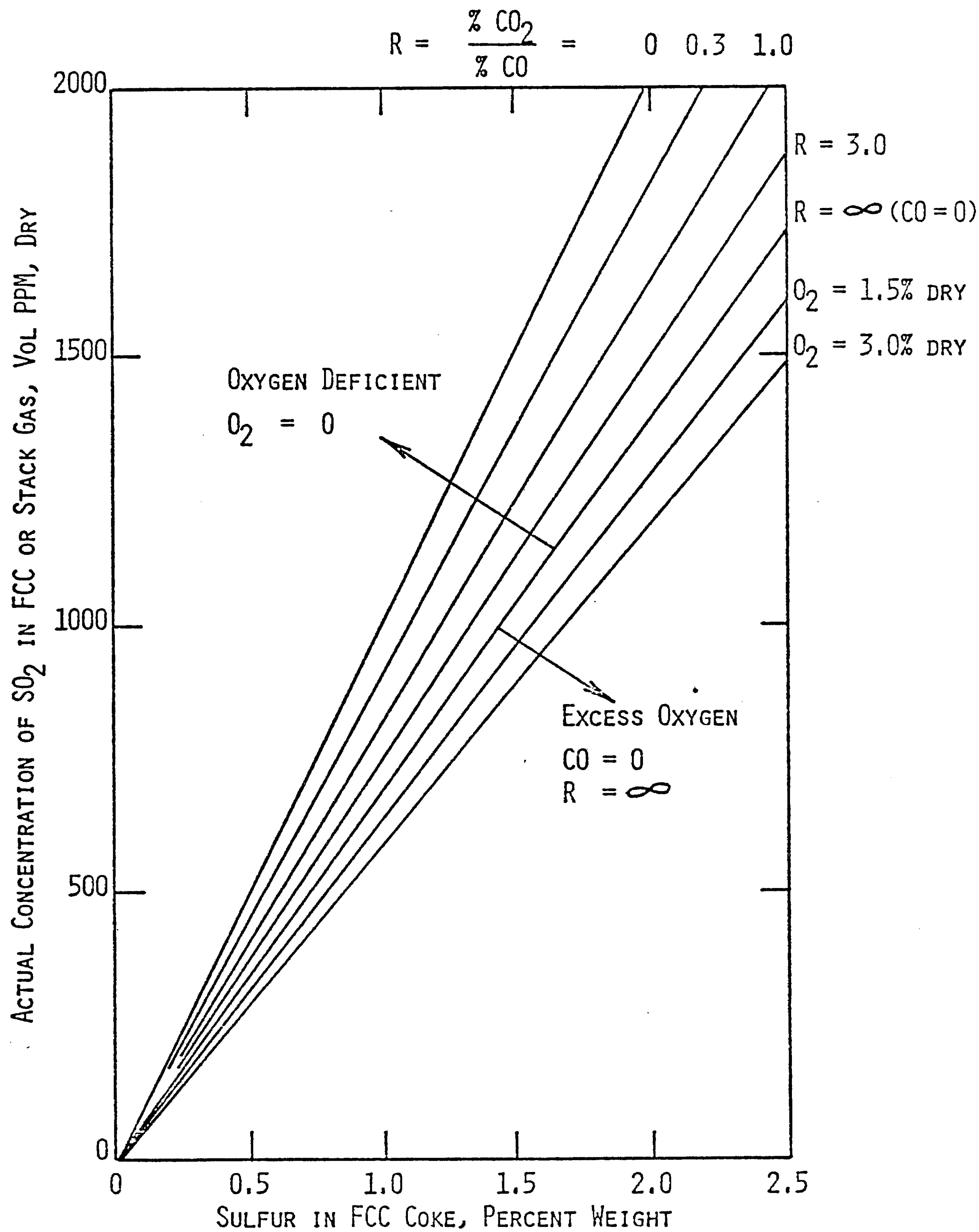

FIGURE H-2. SOx CONCENTRATION IN FCC EXHAUST AS A FUNCTION OF COKE SULFUR

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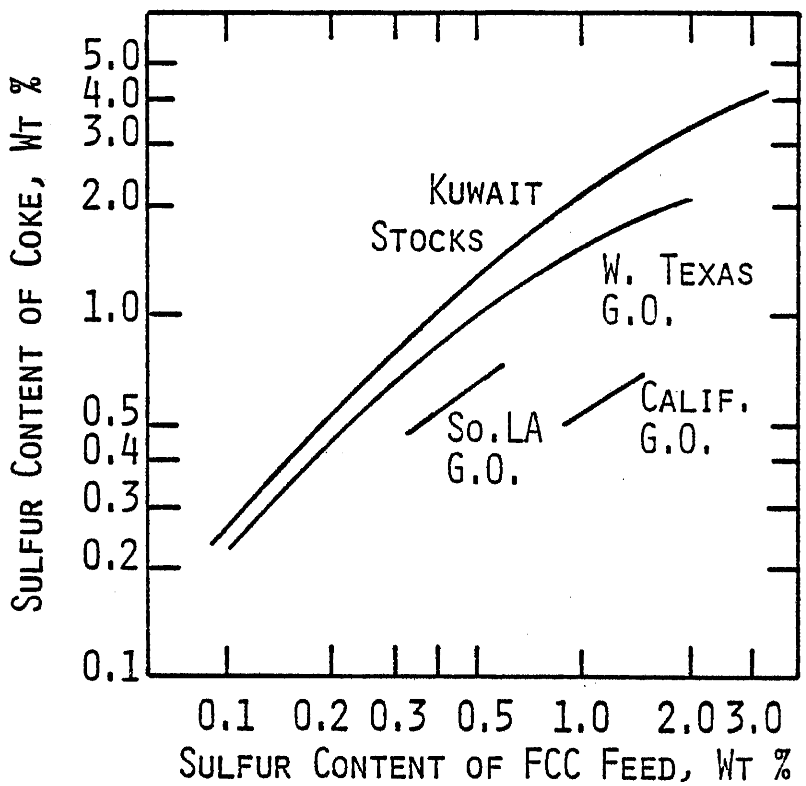

Figure H-3. Sulfur Content of FCC Coke for Desulfurization of Various Gas Oils.

is bound in the oil molecules. Feeds such as California gas oil that are easily desulfurized (Ref. 88) produce lower sulfur coke. The desulfurization process releases the sulfur as hydrogen sulfide and a higher rate of H_2S formation as a percent of fuel sulfur indicates the sulfur is less tightly bound. The unfortunate conclusion is that the crude stocks with the highest sulfur content appear to be those in which the sulfur is most tightly bound. No specific information could be uncovered that fully explains this effect with sufficient confidence to be able to predict coke sulfur levels in terms of feed properties. FCC process research in the past has been mostly concentrated on increased gasoline yield and, while it may well be that the coke sulfur process is understood within the proprietary domain, there is no external visibility of such understanding. If this is in fact the case, installation of feed desulfurization equipment would not be reliable or cost effective in the face of rapidly changing crude sources and resulting unpredictable desulfurization capability. Requirements to produce lower sulfur gasoline may change that picture but it would appear that other more confident means must be employed from an FCC emissions control standpoint, and that feed desulfurization does not represent an existing technology for which costs can be established reasonably well. These alternatives are discussed in Section H-5.

H-3.0 MEASUREMENT OF SOx EMISSION FROM REFINERY FCC UNITS

Six of the eight Basin FCC units were offered for test during this program. These units were found to be well furnished with accessible test sample ports at the stack exit of the CO boilers. Samples at positions upstream of the CO boilers were not taken as most units were not provided with adequate sample ports and stack exit emissions were the primary requirement. A limited amount of process data was made available. Tests were conducted with the methods and procedures outlined in Appendix D.

The FCC process is such that it would be expected that gas concentrations would be quite steady with little fluctuation allowing accurate data to be taken. For most units, the recordings of SO_2 and O_2 were quite steady but in one case, cyclic fluctuations were observed. This fluctuation had a time period of about 15 minutes and was not expected or explainable by the plant operators. The simultaneous increase of SOx and decrease of O_2 suggests a control cycling on air supply at some point in the system. Air is supplied to both the FCC unit and CO boiler and instruments on these supplies indicated steady flows. As SOx wet chemistry measurements were taken over a period of about 20-30 minutes, these cycles should be averaged out in the measurements.

Two other facts are pertinent to the test results. All test samples with one exception, were taken from CO boiler stacks. The exception was one FCC that exhausted through a precipitator after which the flow was split with one part passed through a CO boiler. Apparently steam requirements are less than obtainable from full FCC CO gas heat content and the excess flow is incinerated in a gas-fired thermal oxidizer. The main difference in the two stack effluents is that for the CO boiler, temperatures are 550-750°F while the thermal oxidizer stack temperature is about 1600-1700°F.

The second pertinent fact is that one FCC unit operates with the sulfur plant exhaust injected into the FCC exhaust. FCC feed is desulfurized with the objective of resultant emissions that are less than operation of the FCC without desulfurization plus use of a tailgas unit on the sulfur plant. During tests of this unit, SO_2 concentrations were initially observed to be over 1200 ppm. This high level was traced to a non-optimum air rate in the sulfur plant. When this air rate was properly adjusted, SO_2 concentrations were reduced below 500 ppm. Control systems in sulfur plants are discussed in Appendix I.

Test results for the averages of three wet chemistry samples are presented in Table H-I. Tests indicated all units with one exception were operating under 500 ppm ranging from 213 to 588 ppm of SOx. SO_3 concentrations varied from 3 to 38 ppm with the Shell method and one test with the LA APCD method indicated no SO_3. The test methods are discussed in Appendix D.

SO_2 concentrations as a function of flue gas stack flow are shown in Figure H-4 with an average of 405 ppm. This average is identical for both the LA APCD data and the data of this program. There is no trend of concentration apparent with unit size. Also shown are data taken from LA APCD source tests (Ref. 89). The data scatter is to be expected in light of the process variations discussed in Section H-2. The dashed line surrounding the data indicates the range of conditions required to assess stack gas sulfur removal and illustrates the very wide range in concentration and flow that must be dealt with.

A more reasonable correlation was obtained on the basis of emission factors related by lb SOx as SO_2 per 1000 barrels of feed as shown in Figure H-5. Shown are the data from LA APCD source tests and the current program. The emission factor of 525 lb SO_2/1000 BBL recommended by EPA is about 25-30% higher than the source test results. The agreement between the LA APCD data and the current program is quite consistent. In view of this agreement, the average emission factor of 405 lb SO_2/1000 BBL obtained was used for inventory of all the Basin FCC units. Use of a common emission factor was felt to be a more reasonable approach in view of process variability as opposed to inventory of each unit at the test emission rate. (The numerical equality of 405 for average ppm and emission factor has no particular significance.)

TABLE H-I

SUMMARY OF REFINERY FCC TESTS

Test No.	Process Rate BPD	Stack Flow SCFM (Wet)	Flue Gas Oxygen % (Wet)	Flue Gas Moist. %	SO_2 ppm (Wet)	SO_3 ppm (Wet)	$\frac{SO_3}{SOx}$ % (Vol.)	Emission SO_2 lb/h	Rates SO_3 lb/h	Emission Factor $\frac{lb/SOx}{1000\ BBL}$	SOx Test Method
10-W	51480+	108000*	N/A	11.4	470	0.0	0.0	512.8	0.0	483+	LA
10-E	51480+	108000*	N/A	11.4	442	38.0	7.9	482.1	52.1		Shell
7-1	51000**+	110200*	1.5	12.5	414	3.6	0.9	461.4	4.2	468+	Shell
7-2	51000**+	91500*	3.0	12.5	563	9.0	1.6	520.0	10.5		Shell
11	35000**	143600*	N/A	22.8	367	11.0	2.9	531.8	20.1	376	Shell
13	12900**	51441	1.95	9.5	478	3.6	0.7	248.3	2.4	466	Shell
20	10300	32407	1.4	10.9	420	3.0	0.7	137.5	1.2	323	Shell
22-1	28000**	136490	2.3	15.9	206	7.0	3.3	284.0	12.1	252	Shell

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+ Two stacks, tested separately, one FCC unit

* Stack flow provided by refinery

** Process rate proprietary, rated rate shown

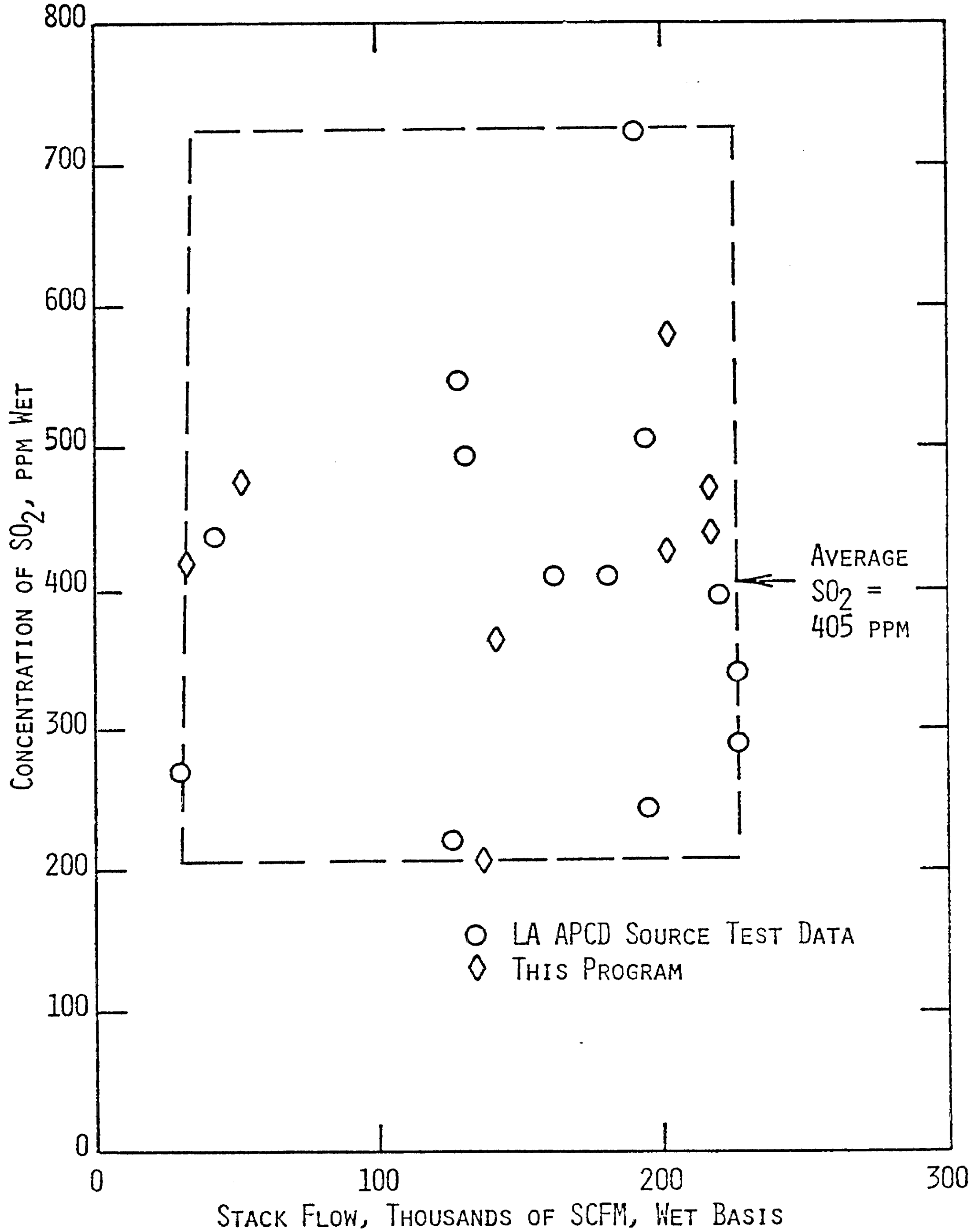

Figure H-4. Refinery Fluid Catalytic Cracking Unit CO Boiler Stack SO_2 Versus Flow.

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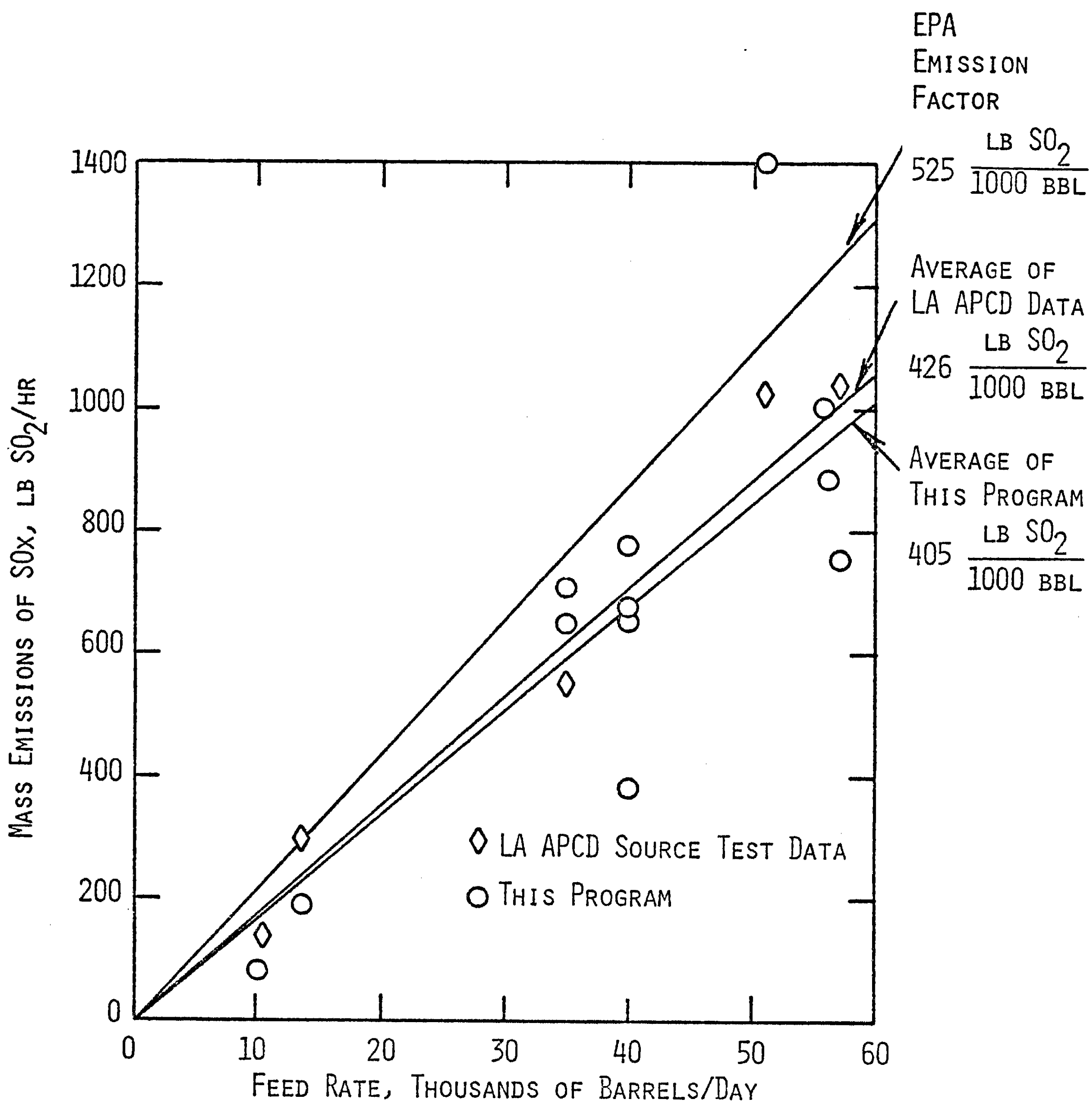

Figure H-5. Refinery Fluid Catalytic Cracking Unit Mass Emission Rate of SOx as SO_2.

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H-4.0 REFINERY FCC UNIT SOx EMISSION INVENTORY

Emissions for the eight Basin refinery FCC units were inventoried on the basis of an average emission factor of 405 lb SOx/1000 BBL. An average percent conversion of SOx to SO_3 was determined from the test data for CO boiler stacks only, as 2.8 percent. It would appear that FCC SO_3 emissions relative to SOx are comparable to that for fuel combustion. Processing rates for 1974 were based on questionnaire data and previous data gathered in the NOx program. Emission rates for summer, winter and annual average daily values were calculated by the methods of Appendix A.

The results of the inventory, presented in Table H-II, indicate FCC emissions of an average of 46 tons/day in 1974. Summer and winter values are slightly higher. Also shown is an SOx emission rate of 62 tons/day that would occur if all units operated at near full capacity. If all units operated 365 days per year, the annual average daily rate at near full capacity would approach the 62 tons/day level.

Projections - Projected SOx emissions to 1980 are estimated based on questionnaire data furnished by the refineries and resultant annual average SOx emissions are projected to be 49 tons/day for 1975 through 1980, essentially similar to the 1974 level. Some refineries were unable to provide projections and in these cases emissions were retained at the estimated 1974 level. The high degree of uncertainty in future crude properties and process variability reflect in a high uncertainty in this projection. Operation of all units at full stack flow conditions and an average 500 ppm level could increase daily emissions to 75 tons/day. With the currently regulated SOx limits in LA County (Table 2-II) emissions could possibly be higher.

TABLE H-II

INVENTORY OF SOx EMISSIONS FROM REFINERY FCC UNITS

Total FCC Rated Capacity, BPSD	SOx Emission Rates, Tons SOx as SO_2/Day			SO_3 Emission Rates, Tons SO_3 as SO_3/Day		
	Aug.	Dec.	Annual	Aug.	Dec.	Annual
292000	50.1	51.78	45.56	1.75	1.81	1.59

Total FCC stack flow = 1,228,000 SCFM (Wet)

Group average SOx, ppm (test) = 416 ppm (Wet)

SOx emission rate at full continuous stack flow - 65 tons SOx/day

Projected SOx emissions = 49 tons as SOx/day constant 1975-1980

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H-5.0 REFINERY FCC UNIT SOx REDUCTION POTENTIAL

A study conducted for EPA (Ref. 14) defined three potential methods for reduction of SOx emissions from refinery FCC units:

1. Increased stripping steam rate
2. Feed desulfurization
3. Flue gas desulfurization

Methods 2 and 3 are methods currently operating or proposed for fuel burning devices. Method 1 is unique to the FCC process and was discussed in Section H-2 in relation to the whole process. Normal FCC steam stripping rates range from 0.2 to 1.0 lb steam per 100 lb catalyst flow (.2 to 1.0% weight of catalyst flow). In initial analysis of Ref. 14, it was estimated that if steam stripping rates could be increased to 4-5% weight, SOx emission of 2000 ppm could be reduced to 200 ppm. This would require one of several optional methods to handle the increased steam flow to prevent product deterioration.

A second phase of this study (Ref. 90) involved a laboratory scale evaluation of steam stripping effectiveness in removal of sulfur from actual spent catalyst obtained from refineries. The test fixture was a semi-fluidized system not very representative of an actual system. The test results indicate that steam stripping is not nearly as effective as originally believed. Results were highly catalyst dependent and steam flows of up to 100% of catalyst flow rate were tested in an attempt to extend the method to the 200 ppm level. It appears that the most reasonable SOx reduction that could be achieved is about 25%. Steam-to-catalyst percent varies from about 5 to 50% with catalyst type to achieve a 25% reduction. The method therefore does not appear attractive for high SOx units. However, as a means of reducing Basin FCC units from a current average of just over 400 ppm down to a level equivalent to burning of 0.5% sulfur oil (315 ppm) such a method could offer promise. Cost estimates were generated (Ref. 90) for the steam stripping process to augment previous cost estimates presented in the Phase I study. These cost estimates are based on two levels of catalyst/oil (C/O) weight flow ratios of 6 as "typical" and 12 as a "worst" case. Investment costs are about 50% greater for the C/O of 12. Basin FCC units are believed to operate in the range of 6 to 8 C/O. Using the cost data in Ref. 50 for the C/O of 6 and a steam stripping rate of 6% lb steam/lb catalyst, the investment costs (July, 75 basis)* range from $900,000 at the 13,000 BPD size to $2,500,000 for the 57,000 BPD size. Total cost for the 7 major Basin FCC units would be $13,400,000. Operating costs based on the economic assumptions in Refs. 14, 50 would range from .12 $/BBL processed for largest units up to .17 $/BBL for the smallest. Reductions achieved would be only about 11 tons/day with an average cost/benefit ratio of 3185 $/ton of SOx reduced.

Reference 14 also presents cost estimates for feed hydrodesulfurization and flue gas desulfurization (FGD).

FCC feed hydrodesulfurization was found most expensive of the three methods. The capital costs range is $5 to 21 million for a total of $113 million and operating costs were .80 to 0.48 $/BBL for 13-57 k BPD range based on a 3.36% to 0.243% feed sulfur reduction for 200 ppm SOx exhaust. (Based on the Gulf data (Ref. 88) it is unlikely that this reduction would actually be achieved.) Basin FCC units emission average of 416 ppm SOx would indicate a coke sulfur content, by Equation H-3 with 1.5% O_2, of about 0.65%. Further, assuming feed is California gas oil, Ref. 88 would indicate a feed sulfur is about 1% at this coke sulfur level. To reduce coke sulfur to an emmission level equivalent to burning 0.5% sulfur oil fuel, it is estimated that FCC feed would have to be desulfurized to about 0.7% to achieve an 0.48% coke with adequate margin. Adjusting the cost figures of Ref. 14 to this level (mainly reduced hydrogen cost), the operating cost range is 0.72 to 0.43 $/BBL for a total Basin FCC SOx reduction of 12 tons/day at a cost/benefit ratio of 17000 and 11030 $/ton for the 13-57 k BPD range. These cost/benefit ratio numbers are about 3 times higher than the steam stripping method at 3185 $/ton. Further feed desulfurization to 0.1% would incur higher hydrogen costs increasing operating cost range to 0.80 and 0.48 $/BBL. Coke sulfur

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*All costs in this section are adjusted to July, 1975 by the Chemical Engineering Plant Cost Index of 182.

would be reduced to about 0.15% producing a stack concentration of 97 ppm. The result would be a 31-tons/day total reduction (70% reduction from 44 tons/day) at a cost/benefit ratio range of 6345 to 4387 \$/ton.

Flue gas desulfurization (FGD) was considered in Ref. 14 with a screening conducted of over 100 processes. Costs were evaluated for six processes and the Westvaco process was clearly identified as the most economical. The other process included a Shell process, Wellman-Lord, Magnesium Oxide, CAT-OX and a Union Carbide molecular sieve process.

The Westvaco FGD process, developed by Westvaco Corporation, Research Center, N. Charleston, South Carolina, utilizes carbon to catalyze conversion of SO_2 to sulfuric acid. The main advantage for refinery installations is that the system uses hydrogen that is normally available in refineries to reduce the H_2SO_4 to sulfur and water or alternately use H_2S, also available in a refinery, to convert the H_2SO_4 to a concentrated stream of SO_2 that can be sent to an existing Claus plant. Cost estimates (Ref. 14) indicate the SO_2 version is cheaper by about 20%. The process is reported capable of being installed either upstream of downstream of the CO boiler but the upstream position is lower cost because of low volume flow. According to Ref. 14, the process is only developed to a 333 CFM pilot stage and therefore does not particularly represent the existing developed technology desired for this program. However, costs for installation on Basin FCC units are presented below.

Westvaco process capital investments adjusted to the 13-57 k BPD range and July, 1975 are 1.8 and 4.9 million dollars and operating costs would be 0.16 to 0.11 \$/BBL. These operating costs are based on a 2000 to 200 ppm reduction (90%) and at that level the cost/benefit ratio would range from 305 \$/ton to 162 \$/ton for the 13-57 k BPD range. Adjustment of these costs to a 500-50 ppm reduction range results in lower operating costs of 0.14 and 0.08 \$/BBL but increases cost/benefit ratio range to 890 to 501 \$/ton for a total Basin FCC unit SOx reduction of 39 tons/day.

At an average cost/benefit ratio of $531, the Westvaco flue gas desulfurization system option is clearly the most cost effective of the three methods evaluated (Ref. 14). This is in contrast to the conclusions of Ref. 14. Prior to laboratory scale tests, conclusions were that steam stripping would be most effective. Capital costs are lower for steam stripping but operating cost is higher and reductions only nominal as Ref. 50 showed.

In view of the apparent attractive cost of the flue gas desulfurization,method investigation was made to determine whether there were any existing FCC units that employ FGD. Such a unit was found to be operating in the Exxon refinery in Baytown, Texas. This sytem, proprietary to Exxon and developed by Exxon Research and Development, Florham Park, New Jersey, consists of a venturi scrubber that removes both catalyst particulate and SO_2. A 300,000 ACFM unit was started up in March 1974 and Exxon reports indicate that 95% SO_2 removal has been achieved (as well as 90% particulate removal). Installation downstream of the CO boiler is recommended. Scrubbing of SO_2 is accomplished with caustic rather than lime or limestone as used in power plant scrubbers and this is reported to eliminate scaling problems. Exxon reports that FCC scrubbing is more attractive than power plants because of flue gas chemistry differences. Cost estimates for installation of this sytem on Basin size FCC units were obtained from Exxon and are summarized in Table H-III. (Ref. 91)

Exxon basic costs were employed to estimate total costs for installation on the seven major FCC units (the one smallest already has feed desulfurization). Material and labor costs were doubled to account for costs unestimated by Exxon as listed in Table H-III. (Conventional estimating would indicate an 80% increment but a 100% increment was taken for a more conservative basis). Total capital cost is $61 million and operating costs range from .240 to .177 $/BBL with an average of 0.194 $/BBL. At a 95% SOx reduction, the cost effectiveness would range from 1380 to 1073 $/ton (13-57 k BPD) and overall is 1144 $/ton for a reduction of 40.5 tons/day.

TABLE H-III

REFINERY FCC VENTURI SCRUBBER FOR SOx REMOVAL

	Capital and Operating Costs		
Size, SCFM	30,000	150,000	222,000
Approx, BPD	10,000	35,000	57,000
Investment cost, $M			
Material and Labor	1.7	4.45	5.6
Operating cost, $M/y			
Utilities	.129	.653	.961
Maintenance	.035	.095	.120
Total	.164	.748	1.081

NOTES:

1) FCC CO boiler exhaust at 550 °F, 14% CO_2, 4% O_2, 17% H_2O, 420 ppm SOx, 95% removal.

2) Material cost includes: flue gas ducting, jet ejector, scrubbing separating vessel, stack, circulation pumps caustic facilities, reheat facilities, and effluent water treating facilities with no solids separation equipment (assumes ESP operating).

3) Costs not included: freight to site, field labor and burden, engineering, contractor fees, sales tax on material, escalation, project contingency, Exxon engineering charges, off-site and utilities (except water system and piping), Exxon royalty, optional Exxon preference items.

4) Costs are U.S. West Coast, second quarter 1975. (Ref. 91)

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Table H-IV summarizes the costs of the four methods discussed for reduction of FCC SOx emissions. The Westvaco process appears to be the most cost effective approach. However, it has not been demonstrated at the full scale level as has the Exxon system and costs may be low. Therefore, the Exxon process is selected as the best existing technology for potential SOx reduction in refinery fluid catalytic cracking units.

Before discarding the steam stripping approach entirely, it should be pointed out that most FCC units have some margin for adjustment of stripping steam flow. The major portion of the SOx reductions achieved in Ref. 90 tests occurred at very low stripping rates. If a given FCC unit were operating just above the level of a given regulation, it might be possible to examine the effect of an increased stripping rate as a means of bringing the unit under regulations. During tests in the current program, a desire was expressed to some refineries to attempt an increase in stripping steam flow. However, one purpose of stripping is to remove hydrocarbons from the catalyst that would cause excess heat to be released in the regenerator with possible catalyst damage and process upset. Because of this safety problem, the refineries were unwilling to allow any adjustments, but this approach might be worth evaluating at any future time should regulation compliance be a problem.

TABLE H-IV

REFINERY FCC POTENTIAL SOx REDUCTION METHODS

Potential Reduction Method	Projected Reduction Tons/Day	Estimated Total Capital Cost $M*	Estimated Average Operating Cost $/BBL (Range)*	Estimated Average C/E Ratio $/Ton (Range)*	Developed Status
Increased Steam Stripping	11	13.4	0.125 (17-11)	3185 (4215-2680)	Laboratory scale
Feed Desulfurization for 300 ppm	12	112.8	0.47 (.72-.43)	10437 (17000-11030)	Currently used in at least one refinery
Feed Desulfurization for 90% Feed S Removal (1%-0.1%)	31	112.8	0.52 (.80-.48)	4382 (6345-4243)	Currently practical, status unknown
Flue Gas Desulfurization, Westvaco Sulfur Process	39	26.6	0.085 (0.13-0.08)	558 (890-501)	20000 cfh sub-scale
Flue Gas Desulfurization, Exxon Scrubber	41	61.0	0.194 (.24-.17)	1144 (1380-1073)	Currently operating at 300000 ACFM on FCC unit

*Range is for 13000 to 57000 BPD units, respectively for 7 major refinery FCC units. $M indicates millions of dollars.

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H-6.0 CONCLUSIONS

Fluid catalytic cracking units operated by oil refineries are one of the major sources of SOx in the Basin, emitting an average of 46 tons/day in the Basin. Projections indicate that this level will remain relatively constant with possible fluctuations up to 60 tons/day if all units are operating at near full capacity. (A new Basin low sulfur fuel oil facility will not include an FCC unit.)

Specific process details were not provided by the refineries to allow assessment of the effect that higher sulfur crudes might have on emissions. Based on emissions data taken, it would appear that Basin units are operating on feed in the range of 1.0% sulfur.

Analysis of potential SOx reduction methods included increased steam stripping, feed desulfurization, and flue gas desulfurization. The most cost effective approach was the Westvaco FGD process of carbon adsorption with operating costs of 0.085 $/BBL and an average C/B ratio of 558. However, as this is only in the pilot stage, a scrubber developed by Exxon appears to be the best available existing technology. Reductions of 41 tons/day of SOx can be achieved at an average cost of 0.194 $/BBL with a cost/benefit ratio ratio of 1144 $/ton reduced.

Future requirements for decreased gasoline sulfur content may force the use of feed desulfurization in which case SOx reduction would be a byproduct benefit. Such a process would be about 3 times more expensive. It is interesting to note that SOx emissions (46 tons/day) are about equal to SOx emissions from Basin motor vehicles (40 tons/day). Most (if not all) of the gasoline consumed in the Basin is produced in part by these units. Insufficient process data are available to determine the added SOx reduction from FCC units that will result from implementation of the California ARB regulations limit gasoline sulfur content to 0.03% but such analysis should be considered.

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APPENDIX I

SULFUR RECOVERY PLANTS

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APPENDIX I

SULFUR RECOVERY PLANTS

I-1.0 INTRODUCTION

Currently there are 19 active sulfur recovery plants in the basin ranging in size from 15 to 150 long tons sulfur/day that are capable of recovering about 1500 long tons of sulfur per day (long ton = 2240 lb). About 1/3 of this is standby capacity and operating units run at a reduced capacity so that in 1974 it is estimated that about 240000 long tons of sulfur were recovered and prevented from creating about 1500 tons of SOx as SO_2/day. Prior to installation of these units the waste gases that they now process were burned in flares.

The Claus process on which these units operate, briefly described in Section 2.0 of this report is about 90-95% efficient and prior to 1973 the 1500 tons/day was reduced to between 100 and 150 tons/day by the presence of these units. As these units then were the largest sources of SOx in the basin, LA APCD Rule 53.2 was implemented on June 30, 1973 to limit emissions to 500 ppm of SOx, 10 ppm H_2S and no more than 200 lb/hr of SOx as SO_2 (2.4 tons SOx/day). The 200 lb/hr limit for a typical 100 long tons/day unit represents a 99% recovery of the sulfur.

To accomplish this level of efficiency the basin refineries installed complex tail gas desulfurization processes that have in fact resulted in substantially greater recovery so that in 1976 when all tail gas units are operating the 3 tons/day estimated emissions will represent an overall system efficiency of 99.8% and with a span of two years a major source of Basin SOx emissions has been eliminated.

Failure of Claus plants or tail gas recovery units could result in significantly increased emissions. However, the larger refineries have at least one backup spare unit each. Smaller refineries generally have only one unit but have redundant controls and special procedures for control of emissions during breakdowns.

I-2.0 MEASUREMENT OF SOx EMISSIONS FROM SULFUR RECOVERY UNITS

Tests were conducted on four sulfur recovery plant stacks. These stacks collected effluent from nine Claus plants. One stack tested had two of three plants in operation with no tail gas unit (construction of replacement tail gas system was in process). The remaining three stacks all had tail gas units. The three tail gas units were of the SCOT (2) and Beavon (1) types. These processes are discussed briefly in Section I-3.0. The uncontrolled system was tested to determine precontrol emissions as a means of verifying the effectiveness of controls as no previous test data were found for this plant.

Selection of the units for test was based on a review of LA APCD source tests and EPA source tests in which extensive data on various pollutants was acquired with gas chromatography (Refs. 92,93, 94). Units tested in this program were ones either not tested by EPA or showed highest emissions.

Prior to installation of tail gas units the sulfur plant exhaust was passed to an incinerator in which all sulfur compounds, primarily H_2S were burned to SO_2 and SO_3. Some of these incinerators still are present and serve as the exhaust stacks for the tail gas units or are used, as originally, whenever there is a tail gas unit failure. (Most refineries have backup tail gas capacity.) For the two SCOT units and the one uncontrolled unit tested the incinerators are in operation for elimination of H_2S and samples were taken at the incinerator outlet. The Beavon unit tested serves four separate Claus plants. Each of these has an incinerator but gases are collected and passed to the single tail gas unit. Test samples were taken in the final stack of the Stretford absorber.

Test results are presented in Table I-I. The uncontrolled unit, Test Number 10-S, indicated 7325 ppm of SO_2. Based on the process rate this represents a Claus process efficiency of 91.6% sulfur recovery,

TABLE I-I

SUMMARY OF TESTS CONDUCTED ON SULFUR RECOVERY PLANTS

Test No.	Number of Claus Plants Operating/ Total per Stack	Sulfur Recovery Rate LT/D	Tail Gas Process	Stack Flow SCFM (wet)	Stack Gas Oxygen % (dry)	Stack Gas Moisture %	SO_2 ppm (wet)	SO_3 ppm (wet)	SO_3/SOx % Vol	Emission Rates SO_2 lb/h	Emission Rates SO_3 lb/h	Emission Factor lb SO_2/S. Ton
10-S	2/3	120	None	25177	--	--	7325	16	0.2	1863	5.1	333
17*	1/1	50*	SCOT+	2843	12.0	10.7	104	3	2.8	3.0	0.1	(1.3)*
18	1/1	12	SCOT+	3721	12.5	4.4	115	4	3.4	4.3	0.2	8
22-2	4/1	--	Beavon	9912	0.5	6.7	5.6	2.3	29.1	0.6	0.3	--

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*Test 17 process rate not available, emission factor based on rating but believed low. Values for SO_2 emissions shown are after closing of bypass valve (prior were over 1500 ppm).

+Test samples taken in incinerator stack.

--Process rate trade secret.

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typical of Claus plant operation (90-95%). The emission rate is 27.4 tons/day. The SCOT process units showed comparable SO_2 and SO_3 emissions at just over 100 ppm. SO_3/SOx of about 3% for an incineration is typical of other combustion processes. During test number 17 initial concentrations were about 1800 ppm and this was traced to an open bypass valve that allowed flow around the tail gas plant. Some operators apparently take samples, for process control, upstream of the bypass entry into the final stack and can therefore be unaware of a leak. This was also observed by EPA during on test (Ref. 92).

Tests of the Beavon system showed the lowest emissions. SO_3% volume level is the highest of all devices tested but measurement accuracy at very low SOx is questionable. Test data taken by the LAC APCD indicated SO_2 and SO_3 to be below the detectable limit and all sulfur to be present as COS or CS_2. Further evaluation, in view of the very low emissions, to establish test method accuracy at low concentrations would not have contributed to significant improvement of the inventory.

I-3.0 SULFUR RECOVERY PLANT SOx EMISSION INVENTORY

Emissions of SOx for the 20 basin sulfur recovery plants were inventoried based on source test data, for units tested, or, for untested units, on the basis of maximum design limit concentrations provided in questionnaire data (Appendix E shows forms). This process insured a conservatively high estimate of the emissions. The emissions of the four uncontrolled plants (3 in one refinery, 1 in a second) were the dominant source emitting about 30 tons/day, as shown in Table I-II, with controlled plants contributing less than 2 tons/day in 1974.

The SO_3 emissions noted in Table I-II are nearly equal for the four uncontrolled units as compared with the 15 controlled units. Tests indicated a low value of only 0.2% SO_3 by volume of total SOx or about 16 ppm on the one uncontrolled unit tested. The SOx inventoried for controlled units is almost entirely due to a 13% by volume conversion of SOx to SO_3 reported by the operators of the 3 Wellman-Lord units. No information on SO_3 was provided in EPA tests.

Projections--Projections were based on projected annual sulfur recovery rates and 1974 emission factors. For uncontrolled units the average emission factor was 330 lb SOx as SO_2 per short ton sulfur produced and for controlled units was 3.8 lb SO_2/short ton, representing a 99% average reduction. Projections include a new 300 ton/day plant employing a Wellman-Lord tail gas unit in a low sulfur fuel refinery addition. Start up date is unknown and may be 1977 rather than 1976 as indicated in Table I-II. The projections indicate that by 1976 these sources will be reduced to only 3 tons/day or only 0.6% of the projected 1976 total of 491 tons/day.

No estimates of emissions increase were made considering the possibility of sulfur plant failures. A brief review of the history of failures indicated that this is not a significant problem from the standpoint of inventory or control strategies.

TABLE I-II

INVENTORY AND PROJECTION OF SOx EMISSIONS FROM BASIN SULFUR RECOVERY PLANTS

Year	Number Inventoried	SOx Emissions tons/day			SO_3 Emissions tons/day		
		Aug.	Dec.	Annual	Aug.	Dec.	Annual
1974	4 Uncontrolled	31.10	30.81	29.56	0.08	0.08	0.07
	15 Controlled	1.64	1.05	1.10	0.15	0.05	0.08
	Total	32.74	31.86	30.66	0.23	0.13	0.15
1975	4 Uncontrolled*			28.92			0.07
	15 Controlled			1.14			0.08
	Total			30.06			0.15
1976	20 Controlled**			2.84			0.13
	20 Controlled**			3.12			0.18

Overall Emission Factors - Uncontrolled = 330 lb SO_2/short ton S

- Controlled = 3.8 lb SO_2/short ton S

*Scheduled control completion late 1975

**Includes 300 ton/day plant at new low sulfur fuel refinery addition, may not actually operate until 1977 or 1978.

I-4.0 SULFUR RECOVERY PLANT REDUCTION METHODS

This section briefly deals with reduction methods rather than potential reductions as very effective controls are already installed. Three control processes have been employed for the Basin sulfur plants:

1. Beavon - Ralph M. Parsons Co.
2. Wellman-Lord - Davy Powergas
3. SCOT - Shell Development

Reference 95 gives a very complete description of these systems and the basic processes will only be touched on here.

The Beavon process consists of two basic stages. In the first stage SO_2 is converted to H_2S by hydrogenation over a catalyst. This H_2S stream is then passed to a Stretford absorber where H_2S is removed from the gas by absorbtion in an alkaline solution. Finally the H_2S is oxidized to water and sulfur in the Stretford solution and the sulfur is extracted by flotation. As the process essentially recovers all sulfur, emissions are not sensitive to Claus plant control of H_2S/SO_2 ratio. Maximum Claus plant recovery occurs at H_2S/SO_2 mole ratio of 2 as shown in Figure I-1. This ratio is a function of H_2S content of the acid gas feed and the air rate in the Claus burner. Older Claus plant control systems maintained a constant acid gas to air flow ratio so that if H_2S content in the acid gas changes the H_2S/SO_2 ratio will shift from optimum. This can result in an uncontrolled unit emitting substantially higher emissions or, in a Claus plant tail gas unit an overloading of the sulfur extraction system. Proper controls and operating procedure have been incorporated to prevent this occurrence and keep the H_2S/SO_2 mole ratio near 2. Adequate capacity is provided to handle any plant upsets.

The Wellman-Lord system utilizes an absorber to extract SO_2 from the flue gas into a sodium sulfite/sodium bisulfite solution. The solution is regenerated in an evaporator-crystallizer where the SO_2 is driven off as concentrated gas that can then be converted to a variety of products or recycled by to the Claus plant inlet.

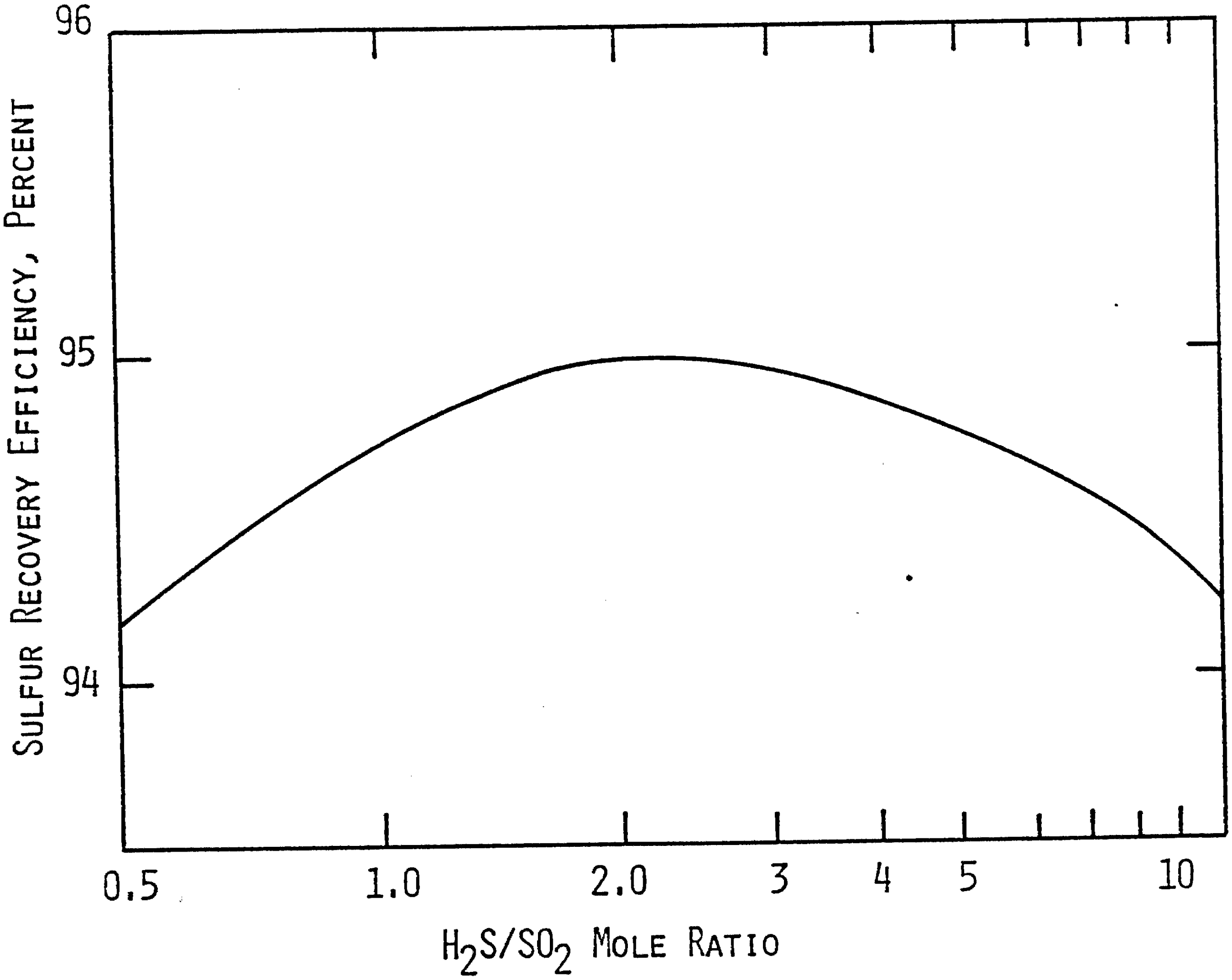

Figure I-1. Theoretical Claus Sulfur Recovery Efficiency Vs. Mole Ratio.

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The SCOT (Shell Claus Offgas Treatment) process consists of an initial reduction process that converts all sulfur compounds to H_2S. Gas containing hydrogen may be necessary to complete this process. The H_2S is then absorbed in an amine section and resultant acid gas is recycled to the Claus plant inlet with no actual sulfur removed in the tail gas unit itself.

As with the Beavon system both of the SCOT and Wellman-Lord systems require improved H_2S/SO_2 mole ratio controls.

Costs from Reference 95 are shown in Table I-III expressed in terms of cost effectiveness for the reductions that have already been achieved in the Basin. Average cost/benefit ratio is estimated at about $235 per ton reduced for a reduction of about 115 tons/day. Not included in these costs are savings that occurred as the result of reduced incinerator fuel consumption. For the Beavon unit with no incineration normally required and fuel costs at $2/MMB there can be a net saving in operating cost from having installed the units. (Capital charges would probably still result in a positive cost effectiveness.)

TABLE I-III

COST EFFECTIVENESS OF SULFUR RECOVERY PLANT
TAIL GAS PROCESS CONTROL SYSTEMS

Tail Gas Process	Rated Capacity LTS/D*	Capital Investment (1) $ M*	Annual Operating Cost (2) $ M/Y*	$\frac{\text{Ton } SO_2}{\text{day}}$ Reduced	C/B Ratio $/ton
Beavon	100	3.15	0.922	13	216
SCOT	100	3.528	1.011	13	237
Wellman-Lord	100	3.294 (3)	1.081	13	253
SCOT	15	1.310	0.356	2	543
Estimated Basin Total	1500	36.0	8.864	115	235

* $M = millions of dollars, LTS/D = long tons of sulfur/day

Notes:

1. Data from Ref. 95, capital costs doubled to account for additional auxiliaries and installation costs; then adjusted to July 1975 with index of 1.26 and capital investment amortized at 20% plus 5% maintenance.

2. Annual costs not adjusted for incinerator fuel reduction that could result in a net saving.

3. Wellman-Lord costs based on 3 units at 150 LT/D scaled to one at 100 LT/D. Common parts used in the 3 units would result in higher actual costs for a single 100 T/D unit. Cost/benefit ratio shown reflects actual installation.

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I-5.0 CONCLUSIONS

The refineries in cooperation with the LA APCD have performed a commendable job in reducing one of the basin's largest sources of SOx emissions. Emissions over the years have been progressively reduced, first, by installation of Claus plants to prevent SOx emissions of over 1500 tons/day and, second, by additional installation of tail gas units to reduce emissions from these plants to less than 3 tons/day when all these programs are completed. At a cost effectiveness of about $235 per ton of SOx for a reduction of a total of 100-150 tons per day these installation represent a very effective method of SOx control that is difficult to achieve in any other area.

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95. Pfeiffer, J. B., Sulfur Removal and Recovery from Industrial Process, American Chemical Society, Advances in Chemistry Series #139, 1975.

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APPENDIX J

SULFURIC ACID PLANTS

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APPENDIX J

SULFURIC ACID PLANTS

J-1.0 INTRODUCTION

Five plants are operated in the basin for production of sulfuric acid of which three were tested. The basic acid making process involves generation of SO_2, oxidation of SO_2 to SO_3 and hydration of SO_3 to H_2SO_4 (sulfuric acid). This is now generally performed in "contact" process units. There are three main sources of sulfur for the basin plants, (1) oil refinery waste gas containing high H_2S concentration, (2) spent acid returned by pipe from refinery alkylation plants and (3) pure sulfur. To process these materials two types of plants are used differing in the source of sulfur. The first is called a "Type S" plant and uses only pure sulfur. The sulfur is melted and burned with air in a burner to form SO_2. The second type of plant, called "wet gas," can operate on any combination of high H_2S gas, dissociated spent sulfuric acid, or molten sulfur all being burned together in a furnace. Following conversion to SO_2 and moisture removal the SO_2 is passed through a multi-stage catalytic converter at temperatures of 700-900°F for oxidation to SO_3. The SO_3 is then absorbed into a stream of sulfuric acid in an absorbing tower.

The only significant source of SOx is the gases that are discharged from the SO_3 absorber than contain unabsorbed SO_2 and SO_3. The conversion process operates at about 90-95% efficiency and in the absence of controls this would result in emissions of 70-140 lb SOx as SO_2 per ton of acid and about 2.5 lb SO_3 per ton. A basic method of control is to add an additional set of catalytic-converter/absorber equipment and this is termed a double conversion/double absorbtion or double contact process. This process, described in detail in Reference , can improve efficiencies to about 99.9%. Other methods of control include electrostatic precipitators, mist eliminators and scrubbers.

J-2.0 MEASUREMENT OF SOx EMISSIONS FROM SULFURIC ACID PLANTS

Three of the basin's five sulfuric acid plants were tested in this program. These three included two double absorbtion acid regeneration plants and one type S sulfur burning plant (only 1 in the basin). One unit has an ammonia scrubber followed by a mist eliminator. One had an electrostatic precipitator and the remaining had a mist eliminator. Samples were taken from existing ports. However in two cases port access and position in the ducting were not considered optimum. Access to ports at the top of exhaust stacks was not possible for safety and construction reasons. For these reasons stack flows may only be approximate and good samples of acid mist particulates may not have been obtained. For the remaining unit sample conditions were excellent.

The data is presented in Table J-I. The first two tests are for double absorbtion units and emissions are well below the LA APCD Rule 53.3 regulation. Emission factors for these two averaged about 4 lb SOx as SO_2 per ton of acid indicating a 99.7% recovery. For the sulfur burning plant the emission factor is higher by a factor of about 3. This unit is capable of operating at substantially higher production rates but runs at reduced capacity to maintain emissions below the 500 ppm level of LA APCD Rule 53.3.

During the preliminary inventory it was suspected that these units might show high acid mist emissions. As the data shows, SO_3 is quite low with percent SO_3 only 1.2 or less of total SOx. This is the result of low stack temperatures that result in good SO_3 condensation and effective removal by the various control devices.

TABLE J-I

SUMMARY OF TEST CONDUCTED ON SULFURIC ACID PLANTS

Test No.	Process Rate tons acid/day	Stack Flow SCFM (wet)	Stack Gas Oxygen % (wet)	Stack Gas Moisture %	SO_2 ppm (wet)	SO_3 ppm (wet)	SO_3/SOx % Vol.	Emission Rates SO_2 lb/h	Emission Rates SO_3 lb/h	Emission Factor lb SO_2/ton acid
4	450 (1)	25510	8.4	1.0	248.1	3.0	1.2	63.9	1.0	3.45
12-1	263 (1)	14907	9.5	5.0	314.2	3.0	0.9	47.1	0.57	4.34
12-2	194 (2)	18524	15.0	0.6	466.0*	1.0*	0.2	87.2	0.24	10.81

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*LA APCD Method, others are Shell

(1) Processes refinery wet gas, double absorbtion process

(2) Burns sulfur only, production rate limited by Rule 53.3 (500 ppm SOx)

J-3.0 SULFURIC ACID PLANT SOx INVENTORY

The three tested units were inventoried on the basis of current test results. A unit essentially identical to that of Test No. 12-1 was inventoried based on that test. The remaining unit, located in a refinery, was inventoried on the basis of previous LA APCD tests and questionnaire data. This unit was not tested because of the five, previous data indicated its emissions were the lowest. Table J-II presents the inventory results and projections based on questionnaire data.

TABLE J-II

SULFURIC ACID PLANT SOx INVENTORY

Plant	Rating t/d	SOx Emissions tons as SO_2/day			SO_3 Emissions tons as SO_3/day
		Aug.	Dec.	Annual	Annual
A	260	0.56	0.39	0.51	0.006
B	300	0.26	0.25	0.21	0.005
C	450	0.74	0.75	0.70	0.011
D	230	0.54	0.40	0.49	0.003
E	180	0.99	0.97	0.73	0.002
1974	1420	2.47	2.47	2.65	0.027
1975				2.94	0.030
1976				2.98	0.030
1980				3.02	0.031

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J-4.0 SULFURIC ACID PLANT SOx REDUCTION POTENTIAL

Emissions of these devices have already been controlled by implementation of LA APCD Rule 53.3 to a level of only 3 tons/day. Prior to these controls emissions are estimated to have been between 50 and 150 tons per day. No cost data was found on which to base the cost effectiveness of these changes.

J-5.0 CONCLUSIONS

As with the sulfur plants a large source of basin SOx emissions has been recently eliminated by installation of effective controls. These controls consisted of basic process modifications that increased production rate but not sufficiently to pay off the installation. Additional scrubbers, precipitators and mist eliminators added are very effective in the elimination of acid mist. No further controls need be considered for these devices.

REFERENCE

96. Browder, T. J., "Modern Sulfuric Acid Technology," Sulfur and SO_2 Developments, American Institute of Chemical Engineers, 1971.

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PETROLEUM COKE KILNS

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APPENDIX K

PETROLEUM COKE KILNS

K-1.0 INTRODUCTION

Petroleum coke is generated in the refining process from the heaviest non-volatile parts of the crude. This material is calcined in five large rotary kilns in the basin to form carbon material that is fabricated into electrodes for the aluminum industry and may also be burned as fuel (but not in the basin except in cement kilns). There are two sources of emissions on these devices. The major one is the calcining kiln exit stack. As shown in Figure K-1 the coke flows countercurrent to a stream of combustion gases that calcin the coke. These gases, containing carbon dust, are passed through an afterburner to ignite the dust and then to a stack where afterburning continues at stack temperatures in the range of 1300-1800°F. The petroleum coke dust, containing about 1-2% sulfur that is burned releases the sulfur to form SO_2 and SO_3. Because of the long times at high temperature the conversion to SO_3 may be expected to be high. As was shown in Figure 2-2, Section 2.0 of this report up to 20% SO_3 by volume could be expected at thermodynamic equilibrium and 1500°F.

The second source of emissions is at the opposite end of the kiln where carbon dust could be emitted. All basin units are controlled at this point with cyclone dust removal equipment and based on LA APCD data the SO_2 emissions at this point are about 1/100 of the rate from the kiln stack.

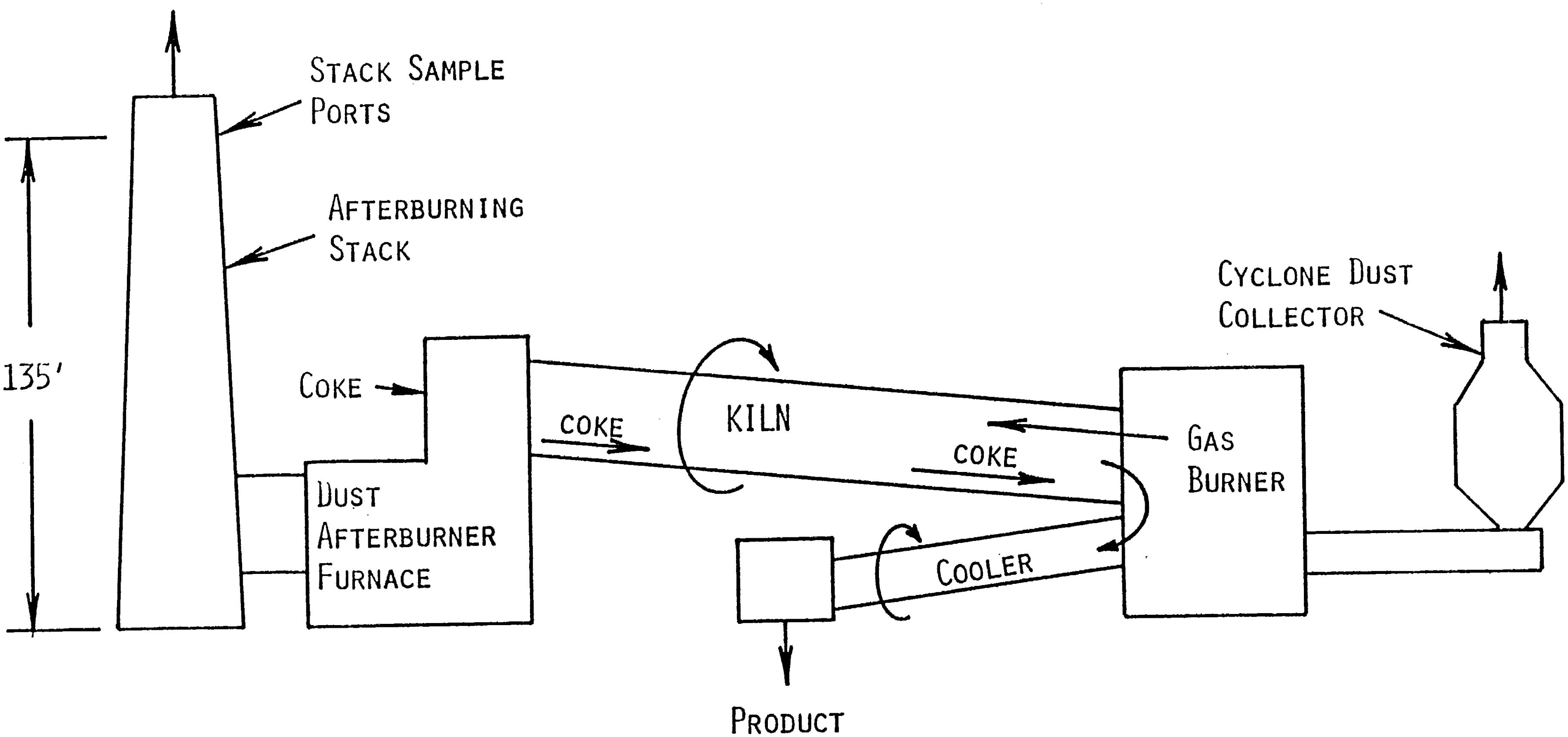

Figure K-1. Petroleum Coke Calcinating Kiln Schematic.

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K-2.0 MEASUREMENT OF SOx EMISSIONS FROM PETROLEUM COKE KILNS

Of the five basin kilns, tests were conducted on two of the larger ones. The high stack temperatures were expected to cause problems with the SOx wet chemistry instrumentation but test showed adequate cooling occurred in sample lines and no particular difficulties were encountered. The results obtained, Table K-I, show that emissions are relatively equal for both kilns with an average emission factor of about 14 lb of SOx as SO_2/ton of coke processed for the Shell method data. Coke sulfur content was reported to be about 1.4% sulfur by weight, capable, if all released, of producing 54 lb of SOx as SO_2/ton coke. The test data therefore indicate that about 26% of the coke sulfur is released as stack SOx. Levels of SO_3 observed averaged about 8.5% by volume of total SOx for the Shell method data. This was the highest percentage level observed for devices where total SOx is in excess of 50 ppm and is believed to be the result of the long time (2-3 seconds) at high stack temperatures. At the SO_3 emission rates, observed this would convert to about 90 lb/h of $H_2SO_4 \cdot 2H_2O$ sulfuric acid particulate mist per kiln of the size tested. The measurements of SO_3 concentration obtained with the Shell-Emeryville Method are about 57% higher than the concentrations obtained with the LA APCD method. Previous LA APCD source tests (Ref. 97) had indicated SO_3 levels of 10-20 ppm. These wet chemistry methods are not readily calibrated so it is difficult to determine which is the more accurate (see Appendix D).

TABLE K-I

SUMMARY OF TESTS CONDUCTED ON PETROLEUM COKE KILNS

Test No.	Process Rate #/h	Stack Flow SCFM (wet)	Stack Gas Oxygen % (dry)	Stack Gas Moisture %	SO_2 ppm (wet)	SO_3 ppm (wet)	$\frac{SO_3}{SO_x}$ % Vol.	Emission Rates SO_2 lb/h	Emission Rates SO_3 lb/h	Emission Factor $\frac{\text{lb } SO_2}{\text{ton coke}}$
5-1	72000	137000	14.0	9.8	363.4*	28.0*	7.2*	503.2*	48.7*	15.1
"	72000	137000	14.0	9.8	310	17.8**	5.4	421.4	31.0	12.4
5-2	72000	128000	14.0	9.8	321.0	34.4	9.7	427.9	57.7	13.2

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*Shell Method, 3 samples

**LA APCD Method, 1 sample only by titration

K-3.0 PETROLEUM COKE KILN SOx EMISSION INVENTORY

The inventory of emissions from petroleum coke kilns was formulated from emission factors obtained from the tests. The two kilns tested were inventoried at the test result emission factors. Another kiln of similar size and two smaller ones were inventoried at the average of test emission factor. The inventory results are presented in Table K-II.

In the preliminary inventory a source of 12 tons SOx/day was included based on the EPA NEDS data base (Ref. 22). This source was classified as a "conveyor." Plant inspection during this program revealed no such source, only the coke kilns themselves, and this source was deleted from the current inventory. The final inventory of 26 tons is less than the preliminary value by only 2 tons. The preliminary inventory included only 16 tons/day from the kilns (plus 12 from the "conveyor") as 72/73 operation of the kilns was much less compared with 1974.

The total of 26 tons of SOx/day represents 8% of basin stationary source SOx emissions. However the 2.7 tons of SO_3/day represents 21% of basin stationary source emissions. These coke kiln emissions of SO_3 are the second largest category, next to utility boilers (see Table 6-II). One of the large coke kilns is about equal in SO_3 emissions to that from the largest basin utility boiler.

<u>Projections</u>--Projections for these kilns is based, for 1975 and 1976, on questionnaire data provided by the operator of four kilns indicating about 80% of 1974 capacity. Very little information was made available on the one remaining kiln. It was not possible to test that kiln for safety and accessibility reasons as the company is in process of installing additional emissions control equipment in the stack area. The impact of this installation on SOx emissions is not known and is not reflected in the projections. Emissions from this kiln were estimated to be 7.5 tons/day of SOx as SO_2 and 0.8 tons/day of SO_3.

TABLE K-II

PETROLEUM COKE KILN SOx EMISSION INVENTORY AND PROJECTIONS

Kiln No.	Rated Coke Rate t/h	SOx Emissions tons as SO_2/day			SO_3 Emissions tons as SO_3/day		
		Aug	Dec	Annual	Aug	Dec	Annual
A	25	4.10	3.70	2.92	0.44	0.39	0.31
B	36	5.67	4.39	5.26	0.60	0.47	0.56
C	36	4.81	5.27	5.10	0.43	0.47	0.46
D	36	5.18	5.12	4.75	0.63	0.62	0.58
E	32	7.92	7.92	7.49	0.84	0.84	0.80
1974	Total	27.68	26.40	25.52	2.94	2.80	2.70
1975	Total	--	--	21.91	--	--	2.32
1976	Total	--	--	21.91	--	--	2.32
1980	Total	--	--	25.52	--	--	2.7

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K-4.0 PETROLEUM COKE KILN REDUCTION POTENTIAL

The source of SOx emissions in these kilns is primarily the petroleum coke dust. These kilns burn both oil and gas. The inventoried emissions are based on about 30% oil use but this oil only contributes about 1 ton of SOx/day to the total emissions. Therefore fuel switching would have little effect on these devices.

Reduction of the petroleum coke sulfur content would be the most direct approach and similar to requiring low sulfur fuel oil. Reduction of the coke to the 0.5% sulfur fuel oil equivalent would produce a 60-75% reduction in emissions. As this coke represent the bottom of the refinery oil barrel it would undoubtedly be the most difficult product to desulfurize. It has been indicated (Ref. 98) that coke can be desulfurized for about $2-3/ton (in 1969). Assuming a 70% reduction in emissions from an emission factor of 13 lb SO_2/ton of coke at $5/ton of coke cost, the cost/benefit ratio would be $1148 per ton of SO_2 reduced and the reduction would be 18 tons of SOx per day.

The only other alternative is stack gas scrubbing. As particulates from these devices could also be high a combined SOx and particulate system would seem to be the best approach and, in fact, is believed to be the approach currently being taken by one basin kiln operator.

While there are a wide variety of scrubbing systems that could be considered one company has listed petroleum coke calciner SO_3 mist, SO_2 and particulate removal at the top of the list of potential applications for packed tower-type ionizing wet scrubber (Ref. 99). Scrubbers modules in the range up to 50,000 ACFM are available and have been in service for over one year. Based on general data of Reference 100 scrubbers of this size cost in the range of $2-6 (July, 75) per actual cubic foot of inlet gas volume or an installed cost of $300,000 per 50,000 ACFM module. (Uncertainities regarding auxiliary and installation costs are high and this cost can only be taken as a very rough estimate without specific knowledge of the installation.) Total flow from the basin coke kilns is estimated at $1.2x10^6$ ACFM requiring about 24 such modules for a total estimated cost of $\$7.2x10^6$. Doubling this cost for auxiliaries and amortizing capital investment at 20% plus 5% maintenance results in an annual cost of $\$3.6x10^6$ for all basin kilns. Operating costs are uncertain but assumed at 30% of annual capital cost typical of other scrubbers the total annual estimated cost would be about $\$4.7x10^6$.

Reductions achieved by this system for SOx removal are not available. Most packed tower scrubbers are quoted at 90% removal and conservatively with an 80% efficiency the total reduction would be 21 tons/day for an overall cost effectiveness of $600 per ton of SOx reduced. Eliminating the one kiln that apparently is already in the process of being reduced, the reduction potential would be reduced to 15 tons/day.

K-5.0 CONCLUSIONS

Petroleum coke kilns are one of the largest basin sources of total SOx and SO_3. SO_3 levels emissions from one kiln, based on current tests, are comparable to emissions from the basin's largest utility boilers. The source of these emissions is coke dust in the gases used to calcin the coke and not primarily from fuel. While sulfur reduction of the coke would be the most direct method of reduction, it appears that the cost effectiveness of this approach would be about $1,150 per ton reduced. Wet scrubbing is seen as the only currently available technology and in addition would reduce particulates. One such kiln is already in the process of such an installation. The cost/benefit ratio of this approach is estimated at $600 per ton for a SOx reduction of 21 tons/day for all five basin kilns, or 15 tons/day for the four kilns not currently undergoing modifications. Although costs are highly uncertain it would appear that the choice of a scrubber would be more cost effective.

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APPENDIX L

METALLURGICAL PLANTS

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APPENDIX L

METALLURGICAL PLANTS

L-1.0 INTRODUCTION

Of the major basin activities, metals production ranks third in emission of SOx, following electric utilities, and the petroleum rated industries. The primary steel industry predominates with sulfur being emitted from coke making ovens, iron ore sintering, and various steel furnaces. Other metals industries with significant emissions are lead and iron scrap reprocessing plants. Total SOx emissions from these industries are estimated to be 45 tons/day and are primarily concentrated in one basin primary steel mill located in San Bernardino County.

L-1.1 Steel Production

Production of steel in the South Coast Air Basin is estimated to cause sulfur oxide emissions in excess of 12000 tons per year as sulfur dioxide. The industry is exceeded by electrical power generation, and petroleum related industries. Most of the sulfur oxide emissions produced by this industry are produced in coke ovens, open hearth furnaces, sinter machines, and power plant boilers burning process gases.

Coke ovens in the South Coast Air Basin produce about 2500 tons/year of sulfur oxides. They burn coke oven gas which has a H_2S content of about 200 grains per 100 cubic foot and blast furnace gas which has a low sulfur content of about 4 grains per 100 cubic foot. Although the SOx is formed by combustion the source of SOx is the coal which the ovens are converting to coke.

Sinter machines are devices which make chunks big enough to be used as blast furnace charge, about walnut size and larger, from fines. A mixture of iron ore and coke fines is burned on a traveling grate. The heat of combustion fuses the iron ore fines into suitable size product.

Sinter machines produce oxides of sulfur. The fuel for the sinter machines is primarily coke breeze and this material would be expected to have a high concentration of fuel sulfur in it. The sulfur is expected to be a source of oxides of sulfur emitted from these devices in addition to sulfur released from the iron ore.

The twelve basin open hearth furnaces produce over 2000 tons of SOx per year. Emissions occur mainly from fuel burned but also from some sulfur in coke and scrap metal added. The furnaces operate over an 8 hour cycle.

Steel mill power plant boilers fired with coke oven gas emit about 2800 tons of SOx per year from sulfur in the fuel. Blast furnaces also emit oxides of sulfur but the blast furnace gas burned in the 8 basin units is low in sulfur content and emissions of 409 tons per year were estimated.

Emissions arise also from a variety of steel furnaces, basic oxygen furnaces, rolling mills, soak pits, and reheat pits. SOx emissions are highest from units burning coke oven gas.

L-1.2 Lead Reprocessing

Two lead plants in Los Angeles County operate four lead melting furnaces. These are used mainly to melt lead scrap from batteries and cables and SOx emissions occur from coke, scrap, fuel and other materials in the charge. Emissions of SOx are about 2000 tons/year.

L-1.3 Iron Reprocessing

One iron cupola was found to be operating in east Los Angeles County. This device melts scrap auto bodies, mixed with coke and limestone and charged to a cupola furnace. SOx emissions occur from coke and scrap. There may be other such devices in the basin but none were identified.

L-2.0 MEASUREMENTS OF SOx EMISSIONS FROM METALLURGICAL PLANTS

Ten basin metals processing devices were tested including two open hearth furnaces at different plants, two lead cupola furnaces, one bank of lead sweating furnaces, one iron cupola, two iron ore sintering machines, one coke oven and one blast furnace (concentration only). The test results are summarized in Table L-I. In all cases samples were taken from existing sample ports.

L-2.1 Open Hearth Furnaces

These devices operate over an 8 hour cycle and sampling was performed through the cycle. SOx emissions were found to be quite low and to occur primarily as a result of fuel burned but some periodic increases in SOx could be observed during the cycle at points where material was added to the melt.

L-2.2 Sinter Machines

Exhaust from these units is passed through baghouses and then underground to tall stacks. Samples for the two units tested were taken at the exit of the baghouse prior to fans that induce air through the baghouses and into the underground stack ducts. SOx concentrations averaged about 250 ppm and stack flows are very high, over 100,000 SCFM. Resultant emissions of SOx were found to be about 300 to 350 lb as SO_2/h with an average emission factor of about 4 lb SO_2/ton sinter. These devices were the largest single source in the metals group.

L-2.3 Coke Ovens

Only one coke oven was tested as emissions occur from burning coke oven gas and therefore are sometimes classified as a combustion source. Knowledge of the coke oven gas sulfur content and flow is sufficient for inventory. The test was conducted primarily to verify quoted coke oven gas sulfur content. Only four of the seven basin coke ovens operate completely on coke oven gas with the remaining burning blast furnace gas with some coke oven gas used.

TABLE L-I

SUMMARY OF TEST RESULTS FOR METALLURGICAL PLANTS

Test No.	Process	Process Rate	Stack Flow SCFM (wet)	Stack Gas Oxygen % (dry)	Stack Gas Moisture %	SO_2 ppm (wet)	SO_3 ppm (wet)	$\frac{SO_2}{SOx}$ % Vol.	Emission Rate SO_2 lb/h	Emission Rate SO_3 lb/h	Emission Factor $\frac{\text{lb } SO_2}{\text{ton}}$
6	Steel Open Hearth Furn.	136,600 lb/heat	15,046	12.0	9.0	18	1.0	5.2	2.7	0.2	Variable
16-1	Lead Cupola	90 t/d	18,242	19.5	2.4	202	2.8	1.4	37.3	0.7	10.2
16-2	Lead Cupola	50 t/d	18,079	19.5	5.2	447	2.9	0.6	84.8	0.7	41.1
16-3	Lead Sweat Furnace	--	--	--	--	0	--	--	0	--	--
19	Iron Cupola	11 t/h	18,872	13.0	6.2	8	3.8	31.1	1.6	0.9	0.25
21-1	Sinter Mach.	1925 t/d	152,377	18.5	7.8	230	4.0	1.7	353	7.7	4.52
21-2	Sinter Mach.	1925 t/d	106,857	19.5	11.1	269	0	0	291	0	3.63
21-CB	Coke Oven	485 t/d	58,769	18.5	11.9	197	4.0	2.0	117	4.7	6.1
21-3	Steel Open Hearth Furn.	500,000 lb/heat	40,561	12.5	11.0	203	4.7	2.3	83.3	2.4	--
21-4	Blast Furn.	1800 t/d	--	10.0	13.0	54	3	5.5	--	--	--

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Samples were taken from ports at the base of the exhaust stack. Test results indicated an emission factor of about 6 lb SO_2/ton of coke. Coke oven gas consumption rate per oven is about 200,000 cubic feet per hour and the measured emissions are equivalent to 220 grains H_2S/100 CF. This reportedly varies between 200 and 300 grains/100 CF.

L-2.4 Blast Furnace

Sample ports consisted only of a 0.25 inch hole in the side of the stack and velocity traverses could not be taken. Samples for wet chemistry were taken and SOx was measured at 57 ppm. Blast furnace gas was reported to contain only 3-4 grains H_2S/100 CF and about 1.5-2 MMCF/h are consummed in each furnace. At that rate emissions would be about 22 lb SO_2/h. Based on combustion of blast furnace gas and 10% oxygen the stack flow should be about 83000 CFM. At that rate the measured 57 ppm SOx would be 48 lb/h of SO_2 reflecting a blast furnace gas sulfur content of about 9 grains/100 CF. This checks closely enough to verify that emissions are as low as expected.

L-2.5 Lead Furnaces

Two lead cupola furnaces and one bank of lead sweat furnaces were tested. Emissions from one cupola were just under 500 ppm and higher than expected by the company's representative. There was no explanation for the higher emissions from one cupola, as both are supposedly charged with a similar batch. As data was reasonably close to previous APCD tests and emissions low no further investigation was made.

Two other lead cupolas operated in the basin were scheduled for test as prior emissions data indicated much higher emissions compared to the two tested with concentrations up to 6000 ppm reported. However, as a result of these higher emissions these units were undergoing additions of scrubbers that prevented access to sample ports and it was decided that tests would not reflect future operations.

The lead sweat furnaces were tested only briefly by means of the SO_2 meter and no SO_2 was indicated. These devices had previously been indicated by others to be in excess of the 2 lb/h cut off in this program but material charged is lead telephone cable and other than natural gas there was no source of sulfur apparent.

L-2.6 Iron Cupola

Tests were taken at a sample port located upstream of a particulate control baghouse. As this baghouse had an open top there was no means to sample at the baghouse exit. This device had previously used petroleum coke at 1% sulfur but now is using regular coke at much lower sulfur content and emissions were found to be about one-fourth previously inventoried levels.

L-3.0 METALLURGICAL PLANT SOx EMISSIONS INVENTORY

Total SOx emissions from metals operations account for about 45 tons/day or 13% of basin emissions. As Table L-II shows these emissions arise primarily from coke ovens, furnaces burning coke oven gas, sinter machines, open hearth furnaces, boilers and lead cupolas, accounting for 95% of the total metals industry emissions. Devices tested were inventoried for the most part based on measurements and questionnaire data. For untested devices the previous LA APCD data was used. Coke ovens, furnaces, and boilers were inventoried based on 220 grains H_2S/100 CF for coke oven gas and 6 grains H_2S/100 CF for blast furnace gas. Open hearth furnace emissions were based on fuel consumption and sulfur content. Steel furnaces and boilers burning coke oven gas were inventoried, for summer and winter emissions, on the basis of burning coke oven gas in the summer and oil in the winter. This results in much lower winter emissions. No specific data were available on actual fuel use patterns. Undoubtedly coke oven gas is burned throughout the year and the summer estimate is believed a more accurate of assessment of emissions.

Projections--Emissions from most of these devices are projected to remain relatively constant at current levels. With the exception of two untested lead furnaces all are within regulation compliance. These two units were projected at a 500 ppm level that is the objective of current abatement controls. The seven boilers do burn some oil but operate primarily on coke oven and blast furnace gas. The curtailment of natural gas may result in increased use of coke oven gas. At 550 Btu/CF a sulfur content of 108 grains H_2S/100 CF (1722 ppm H_2S) is equivalent to burning 0.5% S oil. At the current level of 220 grains H_2S/100 CF (3520 ppm H_2S), burning coke oven gas is equivalent to burning 1.0% S oil. Production of coke may be performed at higher than required rates, as a means of generating fuel needed for other operations when natural gas is not available.

TABLE L-II

INVENTORY OF SOx EMISSIONS FROM METALS PLANTS

Device	Number of Devices	SOx Emissions tons/day Aug.	Dec.	Annual	SO_3 Emissions tons/day Annual
Coke Ovens	7	6.83	5.40	6.93	0.17
Steel Furn./ Coke Oven Gas	13	16.82	8.75	12.60	0.47
Sinter Mach.	2	1.79	0.24	4.37	0.09
Open Hearth Furnaces	12	4.84	4.75	5.47	0.16
Blast Furn.	4	1.13	1.04	1.12	0.08
Boilers	7	11.08	4.26	7.67	0.29
Lead Furn.	4	2.64	5.14	5.40	0.22
Iron Cupola	1	0.02	0.02	0.01	--
Other		0.80	2.90	0.90	0.03
1974 total		45.95	32.50	44.47	1.51
1975				45	1.5
1976				45	1.5
1980				45	1.5

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L-4.0 METALLURGICAL PLANT SOx EMISSIONS REDUCTION POTENTIAL

Steel mill coke oven gas and sinter machine exhaust are the only two areas identified where reductions could be achieved with existing technology. The coke oven gas being used has between 200 and 300 grains H_2S/100 CF sulfur content relative to county regulations of 50 grains/100 CF. Desulfurization of this gas would result in a reduction of 15 to 30 tons/day. Total coke oven gas production is estimated to be about 78 MMCF/day. No specific data was found on costs to desulfurize coke oven gas but costs are estimated to be approximately equivalent to the amine scrubbing gas desulfurization processes used in refineries. At 78 MMCF/day and about 0.6% H_2S such a plant would cost (Ref. 87) about $2.5x10^6$ including off sites resulting in an annual cost of about $800,000. This results in a cost effectiveness of $122 per ton of SOx reduced at a total reduction of 18 tons/day.

Sinter machine reductions could only be achieved with stack gas scrubbing. Stack flows are about 200,000 ACFM per stack. As the sintering process is not unlike the petroleum coke calcining kiln process (Appendix K) at about the same flow, it is probable that the ionizing wet scrubber at $6/ACFM would be acceptable for the sinter machines. Annual cost of such a system was estimated in Appendix K to be $600,000. At 80% removal the cost effectiveness would be $470 per ton reduced for a reduction in SOx of 3.5 tons/day below the current 4.4 tons/day.

With these two approaches the total reduction in the one steel mill would be about 22 tons/day at an annual total cost of $1.4 million and an overall average cost effectiveness of $174 per ton reduced.

L-5.0 CONCLUSIONS

Steel plant emissions are responsible for 45-80% of SOx emissions in San Bernardino County (varying by the amount of coke oven gas burned). These emissions occur from sintering, coke ovens, open hearth furnaces, power plant boilers and other smaller sources for a total of about 40 tons/day in that county. This emissions could be reduced by 22 tons/day with existing technology by desulfurization of coke oven gas to 50 grains/ 100 CF and stack gas scrubbing of the sinter plant exhaust.

Other sources of emissions from the metals industry include lead and iron scrap reprocessing and together emit about 5 tons/day. About half these emissions come from one lead cupola furnace that is currently undergoing scrubber installation and when completed emissions from these sources will be reduced to less than 3 tons/day.

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APPENDIX M

MINERAL PLANTS

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APPENDIX M

MINERAL PLANTS

M-1.0 INTRODUCTION

Basin mineral processing plants include 7 construction aggregate calcining kilns, 26 glass furnaces, 3 gypsum calciners, and 6 cement kilns and these are potential sources of SOx emissions. These plants are estimated to emit about 4 tons/day of SOx and were only 1.2% of total basin emissions in 1974. Glass plants are located mostly in concentrated industrial areas while the aggregate and cement kilns are located in rural areas near mineral deposits.

M-1.1 Aggregate Production

Aggregate plants process silica clay in large rotary gas or oil fired kilns quite similar to cement and coke kilns (see Figure K-1, Appendix K). Clay extracted from deposits is pressed into pellets and charged to the kilns. Samples of clay from one kiln were obtained for analysis and sulfur content was found to vary from 0.35 to 1.0% sulfur by weight indicating a high degree of variability. The sulfur is present in the form of gypsum and the calcining process releases part of this sulfur to form oxides of sulfur in the combustion gases. Tests were originally scheduled for one of these kilns. However the local APCD conducted a test during the same period and those results were reviewed and found satisfactory for inventory purposes. Based on combined results of local APCD source tests the SOx emission from these kilns is 513 tons of SOx as SO_2 per year or 1.4 tons/day. SO_3 emission is 18 tons/year. Of these emissions 69% come from one kiln in Orange County with the remaining from six kilns in Ventura County.

M-1.2 Glass Manufacture

Manufacture of glass in the South Coast Air Basin results in oxides of sulfur emissions as SO_2 of about 786 tons per year. These emissions are from 26 devices and represent about 0.7% of the oxides of sulfur emitted from stationary sources in the South Coast Air Basin. The gas consumption is about 1.3% of the gas consumption in the Basin and almost no oil is used. The major emitters in this industry are 24 glass furnaces or melters as they are called.

Glass is produced by melting a mixture primarily of silica (usually sand), sodium carbonate (soda ash), limestone, salt cake (Na_2SO_4), and other minor additives. Scrap glass called cullet is also added in varying amounts. Glass which may be cut at 200°F is actually brought to about 2750°F in the melter. In order to efficiently produce the product it is necessary to use combustion air which is preheated to a very high temperature. Air preheat temperatures of 1500°F and higher are sometimes used. This is accomplished by bringing the air in through a regenerative air preheater. The preheater is an expanded array of bricks known as checkers. There are checkers on either side of the furnace. The air is brought in through hot checkers, burned with fuel, heats the melt and passes out through the other checkers heating them up. After a time, for instance, 30 minutes, the air flow is reversed and the recently heated checkers warm the air while the hot flue gas rewarm the other checkers. This unit has both a forced draft fan and induced draft fans. The induced draft fans drive ambient air which is passed through a venturi drawing the hot flue gas up the stack.

The desired result of the extensive air preheat is a high flame temperature. One result of long times at high flame and stack temperatures is high percentage emissions of oxides of sulfur as sulfur trioxide.

Salt cake (sodium sulfate, Na_2SO_4), or barium sulfate ($BaSO_4$) are added in small amounts as a flux to increase the rate of melting and prevent scum formation on the surface of the molten pool. The sulfur content of these compounds plus fuels burned is the source of sulfur oxides emissions. Data assembled in the preliminary inventory indicated a high variation in SOx emission factor (0.1 to 4.2 lb SO_2 per ton of glass). These variations were believed due to glass batch formula differences. The amount of sulfate added and percent released were uncertain. There are three basic kinds of glass: (1) flint or transparent, (2) amber colored and (3) green colored. These glasses require different batch formulas and a total of six furnaces were tested that included three flint and three colored glass types. The furnaces selected represent low, medium, and high emission factors. While there are no specific regulations, the maximum sulfate content of the glass furnaces and amount of glass production (called pull rate) is generally limited on the APCD permit as a means of particulate control. One color glass furnace tested had a scrubber installed for particulate control.

M-1.3 Cement Production

Portland cement is made by sintering a mixture of raw materials, one of which is composed mainly of calcium carbonate (as limestone) and the other of aluminum silicates (as clay or shale). During the sintering process chemical reactions take place which produce clinkers of calcium silicates and aluminates. The feed which is a mixture of the above materials is fed into a rotary kiln which is about 500 feet long and 12-16 feet diameter. The kiln turns slowly causing the charge to roll, tumble and gradually move to the discharge (lower) end of the kiln. At the lower end of the kiln it is fired with a gas or oil flame. The combustion air is preheated to 1000°F or higher by direct contact with clinker which has discharged from the kiln. The hot combustion gas and clinker pass counter currently to one another in the kiln resulting in low temperature differences and slow heat transfer. In other words, the combustion gases in a cement kiln are cooled in 500 feet of travel about the same amount that combustion gases are cooled in 50 feet of travel in a boiler. As with other kilns the long time at high temperature offers a potential for high formation rates of sulfur trioxide.

There are six cement kilns in the basin. Four are large and produce grey cement for normal construction and two smaller ones produce white cement for decorative plastering of swimming pools, etc. All are located in the east end of the basin at large limestone deposits.

APCD data had indicated that SOx emissions from cement kilns were negligible even though they burn high sulfur fuel oil. The sulfur is absorbed in the cement clinker and, in fact, sulfur is necessary for proper product formation. The original test plan did not include cement kiln tests. However, one operator has recently converted to coke burning and that kiln was offered for test to determine if the coke resulted in any changes in SOx emissions.

As shown in the next section these kilns act as a very effective "scrubber" removing most of the sulfur from the fuel.

M-1.4 Other Mineral Sources

There are three gypsum calciners in the basin. These units heat gypsum to drive off moisture in preparation for production of construction wall board. As gypsum is calcium sulfate it was possible that sulfur oxides could be emitted. Previous tests had only measured sulfate particulates and did not indicate presence or absence of SOx. One test in this program verified that calciner temperatures are too low for any gypsum to dissociate.

One other source is a rockwool cupola for which previous tests indicated over 1000 ppm of SO_2. Contact with the operator indicated that this unit had been shut down permanently and was not operable for test. No other such devices were located.

M-2.0 MEASUREMENTS OF SOx EMISSIONS FROM MINERAL PLANTS

Mineral plants tested included 6 glass furnaces, 1 cement kiln and 1 gypsum calcining kettle. Samples were taken from existing ports at the top of the stack or near the bottom when stack platforms were not available. The test results are presented in Table M-I.

Results for the gypsum kettle showed undetectable SO_2 or SO_3.

For the cement kiln operating at 2/3 heat input from 2.8% sulfur petroleum coke and 1/3 natural gas the recorded fuel consumption rate was such that 618 lb of SO_2/h could have been emitted during the test. Actual total SOx emissions were only 13.2 lb/h indicating a 97.9% removal of the sulfur. Previous tests were reported to always be greater than 90% removal and these results would tend to confirm that.

Glass furnace tests resulted in a wide range of emission factors from 0.25 to 5.8 lb SOx as SO_2 per ton of glass, confirming the wide range observed in previous data. Also as expected SO_3 as a percent of SOx was high, averaging about 15%. Glass batch mixture data was taken during the tests and measured emissions of sulfur were correlated with the batch sulfur content, primarily as salt cake. Figure M-1 presents the measured SOx emissions as a function of theoretical emissions calculated from the batch sulfur content. The percent of sulfur released varies from 30 to 80% and averages about 43%. This correlation shows three groups of data: (1) one low point for the scrubber unit, (2) several points along the 43% average line and (3) several points near the 100% release line. These correlations help to explain the previous emission factor scatter. No explanation was found for the high point group although there could have been some uncounted sulfur in the batch. Salt cake addition averages only about 5 pounds per ton of cullet free charge and elements minor on a per ton basis can be significant relative to the sulfur content.

TABLE M-1

SUMMARY OF TEST RESULTS FOR MINERAL PLANTS

Test No.	Device Type	Rating t/d	Stack Flow SCFM(wet)	Stack Gas Oxygen %(dry)	Stack Gas Moisture % Vol.	SO_2 PPM (wet)	SO_3 PPM (wet)	SO_3, SOx % Vol.	Emission SO_2 lb/h	Rates SO_3 lb/h	Emission Factor lb SO_2/ton
1	Flint Glass Furnace	239	22,000	8.0	9.0	259	8.0	3.0	57.6	2.2	5.78
2-1	Flint Glass Furnace	240	23,000	9.0	9.0	21	3.0	12.7	4.8	0.9	0.55
2-2	Amber Glass Furnace	195	13,000	-	-	11	4.6	29.5	1.4	0.8	0.25
3	Amber Glass Furnace	77	11,443	11.0	11.0	139	9.0	6.1	16.1	1.3	5.34
8.	Gypsum Kettle	240	7,794	-	25.0	0	0	-	0	0	0
9	Flint Glass Furnace	118	15,054	12.5	15.0	15	3.4	20.7	2.3	0.7	0.58
15	Green Glass Furnace	152	16,363	12.5	11.0	45	10.0	18.2	6.8	2.1	1.34
24	Cement Kiln	1056	180,252	-	9.7	6	0.9	12.5	11.5	2.1	0.30

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$$\left(\frac{\text{LB } SO_2}{\text{HR}}\right)_{\text{CALC.}} = \frac{\text{LB SALT CAKE}}{\text{H}} * 0.43$$

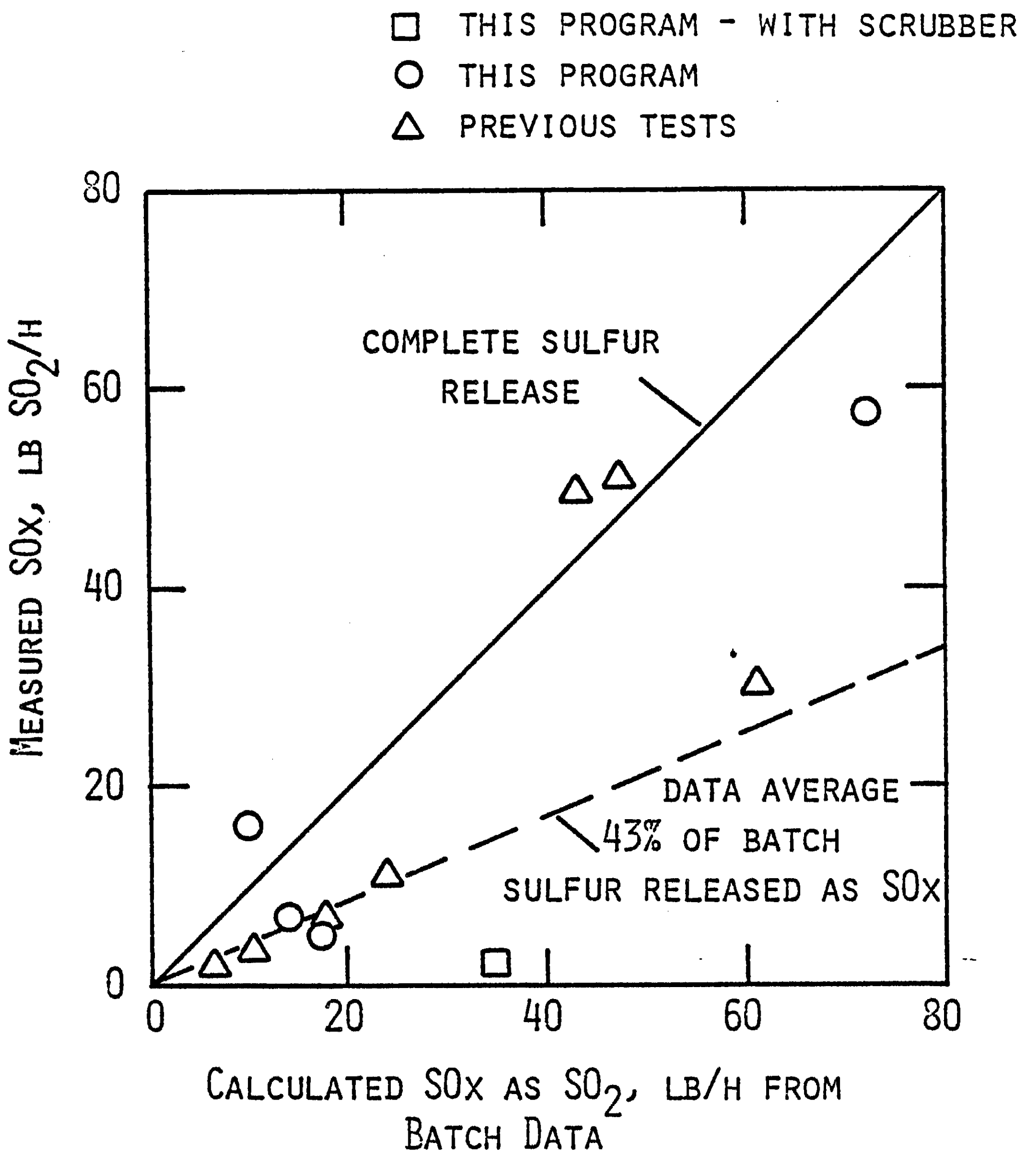

FIGURE M-1. GLASS FURNACE SOx EMISSION VERSUS BATCH SULFUR CONTENT.

M-3.0 MINERAL PLANT SOx EMISSION INVENTORY

Glass furnaces were inventoried on the basis of an average 43% of the batch charge sulfur released as SOx. An overall average emission factor based on current and previous tests of 1.56 lb SOx as SO_2 was used for furnaces where no batch data was available. Seasonal and annual glass production rates from questionnaires were used to determine the glass furnace total emissions shown in Table M-II. These emissions are only 2 tons/day and are very close to preliminary inventory emissions. SO_3 emissions were based on a test values obtained or an average value of 15% by volume for untested devices.

Aggregate kiln emissions estimated in the preliminary inventory were 6.4 tons/day (Appendix C). The preliminary inventory was based, for 6 kilns in Ventura, on the EPA NEDS survey (Ref. 23). Subsequent data furnished by the operator and based on previous source tests resulted in a lower inventory of only 1.4 tons/day from the aggregate kilns.

Emissions projections, based on questionnaire data, indicate no essential changes in emissions from material processing and all increases shown in Table M-II are the result of increased fuel oil burning in glass furnaces and aggregate kilns.

Although the one test indicated cement kiln SOx removal at 98.7%, all cement kilns were inventoried on the basis of fuel consumed and a 90% sulfur removal. The resultant 0.4-0.5 tons per day shown in the table indicate these kilns are one of the smallest basin sources of SOx.

TABLE M-II

INVENTORY OF SOx EMISSIONS FOR MINERAL PLANTS

Device	Number of Devices	SOx Emissions tons as SO_2/Day			SO_3 Emissions tons as SO_3/Day
		Aug.	Dec.	Annual	Annual
Glass Furnaces	26	2.41	2.19	2.15	0.29
Aggregate Kilns	7	1.25	1.39	1.41	0.05
Cement Kilns	6	0.52	0.55	0.36	0.04
1974 Total		4.18	4.13	3.92	0.38
1975				5	0.5
1976				7	0.7
1979 - new supply				10	1.0
1979 - no new supply				10	1.0
1980 - new supply				7	0.7
1980 - no new supply				10	1.0

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M-4.0 MINERAL PLANT SOx REDUCTION POTENTIAL

All mineral plants are operating within current regulations of less than 500 ppm of SOx. Emissions from all these devices together total only 1.2% of basin emissions and no reductions are apparently required.

The one glass furnace tested with a scrubber showed very effective control of SOx. Data on this scrubber (Ref. 100) indicates a rated flow of 43,200 ACFM and at $6 per ACFM the cost is about $260,000 (July 1975) for an annual cost of about $65,000 for capital and $20,000 for operating expenses or a total of $85,000 annual cost. The reduction achieved is about 153 tons per year for a cost/benefit ratio of $554 per ton reduced. The primary purpose of this scrubber was for particulates control but at this cost effectiveness level it is also an effective SOx control. However the emissions from the unscrubbed devices are already very low and no further reductions, from an SOx standpoint, should be necessary for glass furnaces.

One aggregate kiln also has a scrubber installed. This unit is a large horizontal spray chamber with lime injection. No cost data or scrubber efficiencies were available but based on reported stack flows the cost is estimated to be between $200,000 and $600,000.

These two mineral plant scrubbers indicate that technology is available for cost effective control of SOx should such requirements become necessary.

M-5.0 CONCLUSIONS

Mineral plants are responsible for only 1.2% of basin SOx emissions. Glass furnaces contribute about one half these emissions at a rate of about 2-2.5 tons per day. Aggregate kilns emit 1.2 to 1.4 tons/day and cement kilns are less than 0.5 tons/day. Gypsum kettles contribute no gaseous SOx emissions.

Cost effective scrubbers are available for these devices but at this time these are small sources and no further reductions should be considered.

REFERENCES

23. "Point Source Emissions Inventory for California - Exclusing Los Angeles County," EPA Basic Ordering Agreement 68-02-1004, Task 1; Pacific Environmental Services, A. Stein, February 1974.

100. McIlvaine, R. W., "The McIlvaine Scrubber Manual," McIlvaine Co., 1975.

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APPENDIX N

ANALYSIS OF BASIN GAS SUPPLY

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APPENDIX N

ANALYSIS OF BASIN GAS SUPPLY

N-1.0 INTRODUCTION

This appendix presents an analysis of gas supplies in Southern California in comparison with the fuel usages inventoried in the current study. Inventory by summation of individual device fuel consumptions and by overall gas sales and curtailment are two alternate approaches to estimation of Basin SOx emissions.

In reviewing these comparisons it is important to note that not all natural gas sold by gas companies is burned as fuel. Some portion, particularly as used by oil refineries, ammonia plants, and petrochemical plants, is used as feed stock for processes requiring methane or other hydrocarbons. On this basis, one would expect inventoried fuel consumptions to fall short of gas supplied. Also this implies that all gas curtailed is not necessarily replaced with fuel oil burning. Unfortunately there is no specific data available to estimate these differences.

The main source of data for this analysis was the 1975 California Gas Report (Ref. 40). Analysis of the reported data involves estimation of the portion of total Southern California gas that is supplied to the South Coast Air Basin. Three other sources of data were used:

1. Retail gas sales tabulations by air basin obtained from the Southern California Gas Company (SCGC).

2. Tabulation of Utility and Industrial Interruptible gas supplies divided into that supplied to San Diego Gas and Electric Company and all other SCGC customers. This data was provided by the California Air Resources Board Staff.

3. Fuel usage reports provided by the Los Angeles (Metropolitan) Air Pollution Control District.

N-2.0 GAS SUPPLIES FOR 1974

The various sources of data on gas requirements, curtailments and supplies were compared to resolve apparent differences as a means of obtaining a fuller understanding of basin gas distribution.

The first comparison was made to resolve differences in Industrial Interruptible gas as tabulated in the 1975 Gas Report (Ref. 40) and tabulations furnished by SCGC to the ARB staff. These differences were found to lie in the gas that is sold by SCGC to the City of Long Beach. This gas is reported as "wholesale" in the 1975 Gas Report but that category also includes gas sold to San Diego Gas and Electric Company.

Table N-I presents 1974 gas data from the 1975 Gas Report for the Pacific Lighting Companies, The City of Long Beach (LB), and San Diego Gas and Electric Company (SDG&E). Pacific Lighting Companies (PL) consists of Pacific Lighting Service Company (PLS) and Southern California Gas Company (SCGC). The table shows, for example, 224285 MMCF (line 23) of Industrial Interruptible gas requirement for PL. However, also shown is 80162 MMCF of wholesale requirement (line 28). Part of this wholesale requirement goes to LB and is subsequently sold to industrial and utility customers and therefore is burned in the Basin.

Table N-II presents the breakdown of the PL wholesale for firm and interruptible supplies. This breakdown was obtained from the 1975 gas report together with tabulations showing SCGC supplies to SDG&E. The values in the second column are those needed for interpretation of differences between the 1975 Gas Report and data tabulations provided to the ARB by SCGC.

TABLE N-I

ANNUAL GAS SUPPLY AND SENDOUT - MMCF

Line		Pacific Lighting Companies 1974	City of Long Beach 1974	San Diego Gas & Electric Company 1974	Line
	GAS SUPPLY TAKEN				
	California Source Gas				
1.	Regular Purchases	32,125	7,803	176	1.
2.	Emergency Purchases	--	--	--	2.
3.	Received for Exchange	32,498	--	--	3.
4.	Total California Source Gas	64,623	7,803	176	4.
5.	Purchases from Other Utilities	4,504	13,033	79,986	5.
	Out-of-State Gas				
6.	Federal Offshore	5,407	--	--	6.
7.	El Paso Natural Gas Company	597,476	--	--	7.
8.	Pacific Gas Transmission Company	--	--	--	8.
9.	Transwestern Pipeline Company	240,248	--	--	9.
10.	Total Out-of-State Gas	843,131	--	--	10.
11.	Subtotal	912,258	20,836	80,162	11.
12.	Underground and LNG Storage Withdrawal	42,073	--	530	12.
13.	Standby Gas (LPG)	--	--	--	13.
14.	Total Gas Supply Taken	954,331	20,836	80,692	14.
	REQUIREMENTS (Sendout Plus Curtailment)				
	Firm				
15.	Retail Sales	420,226	11,821	41,952 (1)	15.
16.	Special Producer Exchange and Payback	1,712	--	--	16.
17.	Exchange with Other Utilities	5,029	--	--	17.
18.	Wholesale	51,596	--	--	18.
19.	Unaccounted-for and Net Inventory Change	23,713	148	1,481	19.
20.	Company Incidental and Compressor Fuel	7,644	205	418	20.
21.	Subtotal	509,920	12,174	43,851	21.
22.	Underground and LNG Storage Injection	78,205	--	639	22.
	Interruptible				
23.	Industrial	224,285	5,729	7,262 (2)	23.
24.	Oil Company Exchange and Payback	39,755	--	--	24.
25.	Exchange with Other Utilities	--	--	--	25.
26.	Company's Own Plants	--	--	74,572	26.
27.	Other Steam Electric Plants, Retail	373,040	3,052	--	27.
28.	Wholesale	80,162	--	5 (2)	28.
29.	Subtotal	717,242	8,781	81,839	29.
30.	Total Sendout plus Curtailment (21+22+29)	1,305,367	20,955	126,329	30.
	CURTAILMENT				
31.	Firm	--	--	--	31.
	Interruptible				
32.	Industrial	32,320	119	171	32.
33.	Oil Company Exchange and Payback	9,552	--	--	33.
34.	Exchange with Other Utilities	--	--	--	34.
35.	Company's Own Plants	--	--	45,466	35.
36.	Other Steam Electric Plants, Retail	270,426	--	--	36.
37.	Wholesale	38,738	--	--	37.
38.	Subtotal	351,036	119	45,637	38.
39.	Total Curtailment (31+38)	351,036	119	45,637	39.
	GAS SENDOUT				
40.	Firm Excluding Underground and LNG Storage Injection (21-31)	509,920	12,174	43,851	40.
41.	Underground and LNG Storage Injection (22)	78,205	--	639	41.
42.	Interruptible (29-38)	366,206	8,662	36,202	42.
43.	Gas Sendout Including Underground and LNG Storage Injection (40+41+42)	954,331	20,836	80,692	43.

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TABLE N-II

PACIFIC LIGHTING COMPANIES
DISPOSITION OF WHOLESALE GAS FOR 1974

	1975 Gas Report PL Table	From PL Sent to Long Beach	Other Sources Long Beach	Total Long Beach LB Table	From PL Sent to SDG&E	Other Sources, SDG&E	Total SDG&E SD Table
REQUIREMENTS							
Firm - Wholesale	51,596	7,785	4,389	12,174	4,384	679	44,490
Interruptible - Wholesale							
Industrial	--	3,522	2,207	5,729	7,299	- 37	7,262
Steam Electric	--	4,867	- 1,815	3,052	64,474	10,098	74,572
Total	80,162	8,389	392	8,781	71,773	10,066	81,839
Total - Required	131,758	16,174	4,781	20,955	115,584	10,745	126,329
CURTAILMENTS							
Firm - Wholesale	--	--	--	--	--	--	--
Interruptible - Wholesale							
Industrial	--	64	55	119	231	- 60	171
Steam Electric	--	3,076	-3,076	--	35,367	10,099	45,466
Total	38,738	3,140	-3,022	119	35,598	10,039	45,637
Total - Curtailment	38,738	3,140	-3,022	119	35,598	10,039	45,637
GAS SENDOUT (SALES)							
Firm - Wholesale	51,596	7,785	4,389	12,174	43,811	679	44,490
Interruptible - Wholesale							
Industrial	--	3,457	2,153	5,610	7,068	23	7,091
Steam Electric	--	1,791	1,261	3,052	29,107	- 1	29,106
Total	41,424	5,249	3,414	8,662	36,175	27	36,202
Total - Sales	93,020	13,034	7,803	20,836	79,986	706	80,692

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Actual total industrial interruptible gas involves that tabulated in the Gas Report as "Industrial", that tabulated as "Oil Company Exchange and Payback" and that tabulated as "Wholesale". Table N-III compares the 1975 Gas Report data for Pacific Lighting with the data as tabulated by SCGC for the ARB staff and shows that the City of Long Beach gas received as wholesale from SCGC explains the differences in the tabulations.

The purpose in the SCGC tabulation prepared for the ARB was to estimate Basin gas curtailment as a means of estimating fuel oil burned in the 1969-1980 period. The assumption in the use of that data is that all Pacific Lighting gas not sent to SDG&E is used in the Basin and that this gas includes:

1. "Industrial"
2. Oil Company Exchange and Payback
3. Steam Electric
4. Wholesale to Long Beach

These assumptions are not unreasonable for approximations but further refinements are possible based on the data available. These refinements are:

1. Correction of retail gas supply data to eliminate retail sales outside the Basin.
2. Correction for gas sold to the Imperial Irrigation District (IID), El Centro (not in the South Coast Air Basin).
3. Addition of gas obtained by Long Beach from sources other than Pacific Lighting.

The IID, El Centro, gas is anomolous in that SCGC considers this gas as "Industrial" in the 1975 Gas Report but considers it as "Steam Electric" when tabulated in gas sales reports by air basin.

TABLE N-III

COMPARISON OF 1975 GAS REPORT DATA WITH SCGC DATA PROVIDED TO THE CALIF. ARB FOR INDUSTRIAL INTERRUPTIBLE GAS SUPPLIES Year 1974, in MMCF

1974 Gas Report Line No. (page 54)	1975 Gas Report Pacific Lighting Companies 1974	PL Wholesale to City of Long Beach	Data Tabulated by SCGC and Provided to the California ARB Staff	
REQUIREMENTS				REQUIREMENTS
Interruptible				
23. Industrial	224,285	+ 3,522	277,807	
24. Oil Company Exchange and Payback	39,755		39,755	
Subtotal	264,040		267,562	Regular Interruptions, Excluding SDG&E
27. Other Steam Electric Plant, Retail	373,040	+ 4,867	377,907	Electric Utilities, Excluding SDG&E
Subtotal	637,080		645,469	Total - Interruptible, Excluding SDG&E
28. Wholesale	80,162	- 8,389	71,773	Total - Interruptible Requirements SDG&E
Subtotal	717,242		717,242	Total Interruptible Requirements
CURTAILMENTS				CURTAILMENTS
Interruptible				
32. Industrial	32,320	+ 64	32,384	
33. Oil Company Exchange and Payback	9,552		9,552	
Subtotal	41,872		41,936	Regular Interruptions, Excluding SDG&E
36. Other Steam Electric Plants, Retail	270,426	+ 3,076	273,502	Electric Utilities, Excluding SDG&E
Subtotal	312,298		315,438	Total - Interruptible, Excluding SDG&E
37. Wholesale	38,738	- 3,140	35,598	Total - Interruptible Curtailments, SDG&E
Subtotal	351,036		351,036	Total Interruptible Curtailments
GAS SENDOUT				
42. Interruptible	(366,206)			DELIVERIES
Industrial	191,965	+ 3,457	195,422	
Oil Company Exchange and Payback	30,203		30,203	
Subtotal	222,168		225,626	Regular Interruptible, Excluding SDG&E
Other Steam Electric Plants, Retail	102,614	+ 1,791	104,405	Electric Utilities, Excluding SDG&E
Subtotal	324,782		330,031	Total - Interruptible, Excluding SDG&E
Wholesale	41,424	- 5,249	36,175	Total - Interruptible Deliveries, SDG&E
Subtotal	366,206		366,206	Total Interruptible Deliveries

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Historical sales data is available from SCGC by air basin. However, projections in the 1975 Gas Report are made only for total customers and not by basin. The analysis of historical data can be used as a guide in estimating the fraction of future gas distribution in the basin. Table N-IV presents retail sales data for 1972, 1973, and 1974. Firm gas retail sales in the basin are consistently about 90% of total sales. Interruptible retail sales to oil refineries in the Basin are 82 to 87% of total sales. Other industrial and commercial retail sales in the Basin are about 80% and 86% of the total sales, respectively. Basin sales to steam electric are about 95% with the balance going to the Imperial Irrigation District. These historical fractions are sufficiently constant so that they can be applied to estimate projected Basin sales.

Specific data on actual curtailments by basin are not readily available. There are two options for making projections: (1) assume all curtailment occurs in the Basin (pessimistic regarding SOx) or (2) assume curtailments are in the same proportion as sales (optimistic).

The adjustments discussed above form the basis for projecting Basin gas sales and curtailments from total customer projections contained in the 1975 Gas Report.

Table N-V presents the distribution of natural gas, refinery gas and oil inventoried in this program for the various sources. Inventoried natural gas use can be compared with gas sales and inventoried oil use can be compared with gas curtailment for 1974 as a check on the validity of the inventory and projections based on the inventory.

Before this comparison can be drawn the retail sales data (Table N-IV) need to be augmented with other non-retail sales and Basin gas curtailment data must be estimated. Table N-VI presents

TABLE N-IV

HISTORICAL RETAIL GAS SALES DATA
BY AIR BASIN IN MMCF

	1972	1973	1974
FIRM			
South Coast	392,174	413,334	379,475
Other Basins*	43,555	41,896	40,750
Total	435,729	455,230	420,225
%, SCAB	90.0	90.8	90.3
INTERRUPTIBLE			
Oil Refineries			
South Coast	28,198	23,900	25,872
Other Basins	4,315	5,233	5,688
Total	32,513	29,133	31,560
%, SCAB	86.7	82.0	82.0
Commercial			
South Coast	Combined	Combined	22,012
Other Basins	With	With	3,550
Total	Industrial	Industrial	25,562
%, SCAB			86.1
Industrial			
South Coast	138,851	135,070	102,865
Other Basins	32,938	33,207	27,554
Total	171,789	168,277	130,419
%, SCAB	80.8	80.3	78.9 (80% C + I)
All Oil/Com/Ind, % SCAB	81.8	80.5	80.4
Steam Electric			
South Coast	261,619	137,402	102,449
Southeast Desert	4,777	5,079	4,542
Total	266,396	142,481	106,991
%, SCAB	98.2	96.2	95.8

*Other Basins: San Joaquin Valley AB
South Central Coast AB
Southeast Desert AB

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TABLE N-V

INVENTORIED FUEL USE FOR 1974

		FUEL USE, MMCF			
	Natural Gas	Refinery Gas	Oil	Total, NG + Oil	Level Of Gas Service % Gas
I. COMBUSTION SOURCES					
Boilers - Utility	111,398	--	273,608	385,006	28.9
Refinery	8,132	16,251	3,946	12,078	67.0
Other					
Industrial	32,658	--	1,680	34,338	95.1
Coml./Inst.	15,813	--	1,117	16,930	93.4
Process Heaters - Petroleum	32,895	71,018	9,379	42,274	78.0
Internal Comb. Engines - Refin.	1,869	--	0	1,869	100.0
Other	6,026	--	968	6,994	86.0
Waste Gas Incineration	15,030	--	0	15,030	100.0
Total, Non-Refin., Non-Util.	69,527	--	3,765	73,292	94.9
Total, Refinery	42,896	87,269	13,325	56,221	76.3
Total, Non-Utility	112,423	87,269	17,090	129,513	86.8
Total, Combustion Sources	223,821	87,269	290,698	514,519	43.5
II. MATERIAL PROCESSING SOURCES					
Furnaces and Kilns	28,838	--	6,516	35,354	81.6
Petroleum Catalytic Cracking	0	4,749	350	350	0.0
Sulfur Recovery	--	--	--	--	--
Sulfur Acid	--	--	--	--	--
Miscellaneous - Refinery	250	--	143	393	64.4
Other	6,856	--	67	6,923	99.0
Total, Material Processing	35,944	4,749	7,076	43,020	83.6
Total, All Non-Util., Non-Refin.	105,221	--	10,348	115,569	91.0
Total, All Refinery	43,146	92,018	13,818	56,964	75.7
Total, All Non-Util.	148,367	92,018	24,166	172,533	86.0
Total, All Devices	256,765	92,018	297,774	557,539	46.6

TABLE N-VI

SOUTH COAST AIR BASIN GAS SALES AND CURTAILMENT
Year 1974, in MMCF

	Firm	Interruptible: Commerical	Interruptible: Oil Refineries	Interruptible: Other Industrial	Steam Electric
Retail, All SCGC Customers Per 1975 Gas Report (75GR)					
Req'd	420,266		218,114 (1)	(No breakdown in Gas Report)	379,211 (1)
Curtail.	0		30,529		272,217
Sales	420,266		187,585		106,994
Retail, SCAB					
Req'd	379,475	25,596 (2)	30,084 (2)	119,611 (2)	373,040
Curtail.	0	3,584	4,212	16,746	270,591
Sales (SCGC Reports)	379,475	22,012	25,872	102,865	102,449
Oil Company Exchange and Payback (75GR)					
Req'd	--	--	39,755	--	--
Curtail.	--	--	9,552	--	--
Sales	--	--	30,203	--	--
City of Long Beach (75GR)					
Req'd	12,174	994 (3)	--	4,735 (3)	3,052
Curtail.	0	20	--	99	0
Sales	12,174	974	--	4,636	3,052
Total, SCAB					
Req'd	391,649	26,570	69,838	124,366	376,092
Curtail.	0	3,604	13,763	16,845	270,591
Sales	391,649	22,986	56,075	107,501	105,501
KVB Inventory of Fuel Use					
Total Fuel use	not inventoried	16,930	56,964	98,639	385,006
Oil Use, Equiv. MMCF	--	1,117	13,818	9,231	273,608
Gas Use	--	15,813	43,146	89,408	111,398

NOTES: (1) IID El Centro req'd 6171, curtail. 1791, sales 4380, transferred from Industrial to Steam Electric

(2) Curtailment in Basin = 30,529 x .804 = 24,542, distributed by % sales 15%/17%/68% to coml, oil ref and ind.

(3) Total Long Beach Industrial divided by % SCGC sale to Com'l and Industrial.

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these adjustments. Retail requirements, curtailments and sales in the first three rows were obtained from the 1975 Gas Report (PL, pg. 54). Industrial Interruptible values were reduced by known values for the IID, El Centro, customer and Steam Electric values increased by the same amount to adjust the 1975 Gas Report values to be on a comparable basis with SCGC retail sales data. Retail sales (6th row) are as given in Table N-IV. The total curtailment for all "Industrial" customers (30529 MMCF) includes commercial, refinery and other industrial customers, according to SCGC. This value was reduced to 24542 MMCF to estimate Basin-only curtailment based on sales percentage in the Basin (80.39%). This amount was then distributed to commercial, refinery and other industrial categories on the basis of their respective sales percentages. (This probably is an overestimate of commercial curtailment.) South Coast Air Basin requirements (4th row) are the sum of sales and curtailments. To these estimates of Basin retail supply values are added the Oil Company Exchange and Payback and City of Long Beach values (all assumed for the Basin). The resultant values are estimated Basin total gas requirements, curtailment and sales. Values from the KVB inventory, comparable to the Basin supply values are also shown. Fuel oil use by oil refineries is in close agreement with estimated Basin oil refinery gas curtailment. Inventoried steam electric values are slightly higher than estimated Basin values. For all other values the inventoried fuel use is lower than estimated basin requirements. Total commercial fuel inventoried is only 64% of Basin estimates. This is attributed to the probable existence of a large number of small commercial devices at less than 10 MMBtu/hr (not inventoried) burning only natural gas. Oil use inventoried for commercial is only 30% of estimated curtailment, however, as noted previously estimation of curtailment based on percent sales probably overestimates commercial curtailment. For oil refineries the oil use is in agreement, as noted, but gas use is only 77% of estimated curtailment. As the inventory is based on fuel use reports to LA APCD (for both gas and oil) the additional gas sales were probably used as feed stock in hydrogen generation or the assumption that all Oil Company Exchange and Payback gas goes to the Basin could be wrong (only 82% of sales is in the basin).

In the "other" industrial category, total fuel use inventoried is 79% of estimated requirements but oil use is only 55% of estimated curtailment. The inventoried fuel use was based primarily on 1972-1973 data collected by KVB with questionnaires and the comparison with gas curtailment would indicate that about twice as much oil was burned in 1974. The total discrepancy in fuel oil use for the three non-steam electric interruptible categories is 10046 MMCF, equivalent to 7 tons of SOx per day with 0.5% S fuel or 2% of the inventoried annual SOx emissions of 342 tons/day. More important from a projection standpoint is the discrepancy in total fuel use of 48241 MMCF equivalent to 35 tons/day if 0.5% S fuel oil were burned.

Resolution of these discrepancies is not currently practical based on information now available from the gas suppliers. The only other known source of information is the LA APCD which collects fuel use information from selected industrial firms, mainly large fuel users (other than refineries, separately reported). For January-July 1974, 134 companies were surveyed and for August-December 1974 this was expanded to 293 companies. Fuel reported was 37174 MMCF of natural gas and 160728 barrels of fuel oil (964 MMCF equivalent). Correcting these values to 293 companies for the whole year, results in an estimated 77367 MMCF of gas and 2913 MMCF of oil. These values compare with the KVB inventory values for LA County of 60112 MMCF of gas and 3922 MMCF of oil (excluding refineries and utilities). While short on gas consumption, inventoried oil is 35% higher than oil use reported to LA APCD. A further comparison of LA APCD industrial fuel reports for 1973 and 1974 shows only a 15% increase for 1974 over 1973. It would therefore appear that there is no real justification for an assumption that the KVB inventory of industrial fuel oil burned is 55% of actual oil use as the estimate of curtailment would suggest. In reality, the KVB inventory of fuel oil use may well be low, but the gas curtailment figure is probably higher than actual oil use as industries have options other than use of oil when gas is curtailed. These include reduced production and use of propane or other fuels. Actual oil use undoubtedly falls somewhere between the inventoried oil use and the gas curtailment value. Only detailed company by company survey could resolve these differences.

N-3.0 PROJECTED FUEL CONSUMPTION

As a result of the difficulties discussed in the previous section, projected industrial fuel oil burning was not made on the basis of projected gas curtailments on an absolute value basis. Rather the projections contained in the 1975 Gas Report were used to obtain total fuel requirement growth rates together with projected levels of service. Projections were then made on the basis of 1974 inventoried fuel use applying the growth and level of service values. Levels of service were taken directly from the 1975 Gas Report, page 50. Table N-VII presents the data used to develop the growth rates. The data indicates a 10% growth in overall industrial fuel use between 1974 and 1980. The growth in retail industrial sales is 26% but Oil Company exchange and payback falls by 62%. The 10% growth rate was applied to all industrial sources for which no specific projections had been obtained. Growth in firm sales is about 25 percent (74 to 80). SOx emissions that would result from replacement of curtailed industrial and firm gas with 0.5% S fuel oil are shown. In 1980 with no new gas supplies industrial and firm SOx would be 239 tons/day. Addition of utility (460 T/d), material processing (145 T/d) and mobile sources (90 T/d) results in a potential total of 933 tons/day. This is as compared with the projected 833 tons/day (Figure 7-I, no new supplies). The difference is due to the difference in inventoried fuel use versus gas company data as discussed previously and to the use of 0.25% S fuel for firm source projections. It is likely that those sources would use high quality distillate oil with a sulfur content of 0.2 to 0.3%.

REFERENCES

40. 1975 California Gas Report, Prepared Pursuant to California Public Utilities Commission Decision 62260, September 1, 1974.

TABLE N-VII

SOUTH COAST AIR BASIN PROJECTED GAS SUPPLIES
FOR INDUSTRIAL AND FIRM MARKETS
MMCF

	1974	1975	1976	1977	1978	1979 New Supply	1979 No New Supply	1980 New Supply	1980 No New Supply
Interruptible									
Required SCGC Indust. Retail	224,285	243,142	259,915	265,818	271,894	278,301	same	283,352	same
- El Centro, IID	6,171	6,171	6,171	6,171	6,171	6,171		6,171	
Total	218,114	236,691	253,744	259,647	265,723	272,130		277,181	
Basin (80.4%)	175,363	190,524	204,010	208,756	213,641	218,793		222,853	
Oil Co. Ex. & Pay.	39,755	22,354	21,231	18,583	17,231	15,191		15,153	
Long Beach	5,729	5,778	5,795	5,815	5,815	5,851		5,868	
Total, Basin	220,847	218,656	231,036	233,154	236,687	239,834	239,834	243,874	243,874
Growth Re 1974	--	0.99	1.046	1.056	1.072	1.086		1.104	
Level of Service, %	84.5	80	53	40	11	9	0	45	0
Gas Sendout	186,617	174,925	122,449	93,261	26,035	21,585	0	109,743	0
Gas Curtailment	34,231	43,731	108,586	139,892	210,651	218,249	239,834	134,131	243,874
SOx Emissions @ 0.5% S fuel	25	32	79	102	154	159	175	98	178
Firm									
Required SCGC, total	420,226	450,037	463,942	479,547	495,978	512,849		529,904	
Basin (90%)	378,203	405,033	417,548	431,592	446,380	461,564		476,914	
Long Beach	12,174	12,226	12,315	12,311	12,354	12,397		12,487	
Total, Basin	390,377	417,259	429,863	443,903	478,734	473,961	same	489,401	same
Growth Re 1974	--	1.07	1.10	1.14	1.18	1.21		1.25	
Level of Service	100	100	100	100	100	100	93		83
Gas Sendout	390,377	412,259	429,863	443,903	478,734	473,961	440,784		406,202
Gas Curtailment	0	0	0	0	0	0	33,177	0	83,198
SOx Emissions @ 0.5% S							24		60.6

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